# This Page Is Inserted by IFW Operations and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

# IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

		A Service Control of the Control of		•	F-			7.3		7
		<b>a</b> :			25			**		
					*		No.		enter	- 1
· ·									The Park	* 4
					1 - 4 - · · · · · · · · · · · · · · · · ·	4,				•
				1		4.		_ <b>*</b>		
2				1						
		·	i ali	· · · · · · · · · · · · · · · · · · ·		F 1				
- 's						, s, 3, 2				
				i			*			
·				· · · · · · · · · · · · · · · · · · ·						
			( F.					4		
,					٠		٠.	¥		
										,
			A . 19			*2 - 2	.7:			
		X	•							
	y									
	* .			•						
		×								
	Ac.	5°		2						
		·		# - 1 · 1						
					***					
				. 2						
			-		A					
*.					4.9					
	10	•								
		i.								
		. ************************************					· ·			
		****								
		***								
		20 Vin								
	ž.				€ <b>.</b>					
	*	200 20			e it is	**				
	*	200 20			e it is	**				
	ж 					* * * * * * * * * * * * * * * * * * *				
						* * * * * * * * * * * * * * * * * * *				
						* * * * * * * * * * * * * * * * * * *				
						* * * * * * * * * * * * * * * * * * *				

### **PCT**

## WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



### INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7:
C11D 3/22, 1/62

(11) International Publication Number: WO 00/65015
(43) International Publication Date: 2 November 2000 (02.11.00)

(21) International Application Number: PCT/US00/11056

(22) International Filing Date: 25 April 2000 (25.04.00)

(30) Priority Data: 60/131,288 27 April 1999 (27.04.99) US

(71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

- (75) Inventors/Applicants (for US only): BETTIOL, Jean-Luc, Philippe [FR/BE]; 93, Avenue J, Slegers, B-1200 Brussels (BE). VERSCHUERE, Ann, Katrien, Marie, Agnes [BE/BE]; Asselsstraat 102, B-9031 Drongen (BE). BAECK, Andre, Cesar [BE/BE]; Ptusessteenweg 273, B-2820 Bonheiden (BE). SMETS, Johan [BE/BE]; Bollenberg 79, B-3210 Lubeek (BE). BUSCH, Alfred [DE/DE]; Handelsstraat 210, B-2910 Londerzeel (DE). COOREMANS, Steven, Paul, Georges [BE/BE]; Kasteelstraat 224, B-9255 Buggenhout (BE).
- (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).

(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW). Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

#### Published

Without international search report and to be republished upon receipt of that report.

(54) Title: SURFACE CARE COMPOSITIONS AND METHODS FOR TREATING SURFACES

#### (57) Abstract

The present invention relates to a surface care composition, preferably a fabric care composition to be applied on a new and/or clean surface, preferably fabric surface, fully or in discrete regions thereof, comprising a film-forming polymer and providing superior soil removal performance while maintaining the particulate stain removal performance. The present invention further relates to a process of treating a new and/or clean surface, preferably fabric surface, fully or in discrete regions thereof with such composition, to impart soil release properties thereto.

### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LÜ	Luxembourg	SN	Senegal
ΑU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
ВВ	Barbados	GH	Ghana	, MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Мехісо	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		•
CU.	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

1

# SURFACE CARE COMPOSITIONS AND METHODS FOR TREATING SURFACES

#### Field of the Invention

The present invention relates to a process of treating a new and/or cleaned surface, preferably fabric surface, to impart soil release properties thereto and to the corresponding surface care, preferably fabric care treatment compositions.

#### Background of the invention

Treatments of fibers and fabrics comprised of fibers prior to or after cleaning (washing, dry cleaning, etc.) of such fibers and/or fabrics are known in the textile and fiber/fabric-treating industries. Examples of such known treatments are sizing treatments, which are typically applied to fibers prior to being woven into fabric, and finishing treatments, which are typically applied to fabrics (woven fabrics) or already processed textiles.

Finishing treatments can be permanent, semi-permanent (i.e., more than one, typically more than 2 domestic wash cycles are needed to substantially remove the finishing treatment, in other words reapplication of the finishing treatment is not necessary after each wash) or non-permanent (temporary) (i.e., one domestic wash cycle substantially removes the finishing treatment, in other words, reapplication of the finishing treatment is necessary after each wash). Permanent and/or semi-permanent finishing treatments typically comprise resins. Examples of permanent finishing treatments are permanent press, flame retardation and/or water resistance. Typical permanent finishing treatments

include softening treatments applied to fabrics and/or starching (stiffening) treatments applied to fabrics.

Conventional soil/stain release treatments applied to fabrics have been less than completely effective. Regardless of the cleaning process used (conventional home washing in washing machine, dry-cleaning, etc.) to clean a fabric in need of cleaning, it is not always possible to entirely remove all of the soils and/or stains from the fabric being cleaned. This problem is even more present with today's trend to move to lower wash temperature, lower water consumption and shorter wash cycles, mainly for economic and environmental reasons.

As a result, a frequently observed problem of today's cleaning processes is the incomplete soil and/or stain removal. Some visible examples of such incomplete soil and/or stain removal include, but are not limited to, soil lines, in particular, of body soil and airborne dust left on collars and cuffs of shirts, blouses, T-shirts, soil (e.g., clay) patches on socks (e.g., sports socks), tough food stains (e.g., bacon grease, tomato sauce, meat sauce, etc.), particulate (clay) stains, grass stains, ground soil, and body soil on underwear material. Once the stains and/or soils have not been completely removed from the fabric after the cleaning process (i.e., they have been set on the surface of the fabric or have penetrated the porous regions of the fabric), they are more difficult to remove due to the ageing effect. Therefore, fabrics tend to grey and/or yellow due to the soil deposited and remaining on the fabric. Repetitive use and cleaning of the garment under these conventional cleaning processes increases the intensity of the greying / yellowing to the point ultimately that the garment is unacceptable to the consumer for further use due to its discoloration and/or fading.

Current attempts to solve this problem are frequent re-washing; additional pre-, post-treatment with extra mechanical action or detergent quantity, the use of solvent and/or dry cleaning. However, these solutions result in increased fabric deterioration and/or are more time-consuming and/or less environmentally friendly.

Detergent composition formulators have unsuccessfully attempted to address this problem by formulating detergent compositions with soil release polymers. Such soil release polymers do not wholly prevent the attachment of soil to the fabric but hinder such attachment and renders the cleaning operation more successful. As a result of this hindrance rather than prevention, it is a logical step to increase the level of the soil release polymers in the detergent compositions.

However, by increasing the level of soil release polymers in the detergent compositions, the fabric has a tendency to become stiffer, less desirable in appearance and handfeel characteristics. Thus the upper limit on the amount of soil release polymer is determined by economics and the resulting adverse effect on fabrics, i.e., the appearance and handfeel of the fabric. Fabrics with a relatively heavy application of soil release polymer do not have the same desirable appearance and handfeel as fabrics without soil release polymers. Moreover, it is recognized in the art that the efficiency of soil release polymers differs with fabric type.

Conventionally, fabric care/softness formulators have been more concerned about the "feel", softness and physical properties of the fabrics rather than soil release properties of the fabrics. For example, such formulators have looked at fabric care compositions comprising starch, polyvinyl alcohol and/or cellulose derivatives in combination with other ingredients to impart a smooth surface (i.e., reduced friction) to fabrics during ironing, a moderate feeling and/or skin touch to fabrics, a reduction or depression of wrinkles after washing or drying fabrics, improved tightening of fabrics, body and/or stiffness to the fabrics, and anti-redeposition properties to fabrics.

Moreover, it has been surprisingly found that most of the prior art carbohydrate finishes commonly used in the textile industry or detergent industry in a laundry process or finishing treatment, impart a particulate stain removal negative leading to an actual fixation of stains rather than improved removal. Indeed, without wishing to be bound by theory, it is believed that such conventional carbohydrate finishes have a high affinity for fabric, especially cotton but as well for clay. Such high affinity results in particulate stain removal negative performance.

However, the prior art fails to teach or suggest a silicone- and starch-free fabric care composition and treating process whereby a layer of film-forming polymer with a low affinity for the fabric or other surface is deposited on the fabric surface or other surface (e.g., clothing, fabric curtains, fabric wall papers, fabric tablecloths, fabric napkins, fabric-covered furniture, carpet, upholstery, bed linens, etc.) fully or in discrete regions thereof, prior to and/or after the fabric is cleaned by a conventional cleaning process, and subsequently easily removed by any conventional cleaning process, such as washing and/or dry cleaning.

Accordingly, there is a need for a silicone- and starch-free fabric care composition and treating process employing the fabric care composition whereby a layer of film-forming polymer with a

low affinity for the fabric is deposited on the fabric surface fully or in discrete regions thereof, prior to and/or after the fabric is cleaned by a conventional cleaning process, and subsequently easily removed by any conventional cleaning process, such as washing and/or dry cleaning so that the fabric is protected from stains which would otherwise come into contact with the fabric surface but for the layer of film-forming polymer; a fabric cleaning process that provides superior stain removal performance compared to conventional cleaning processes; a fabric treating process whereby the fabric is imparted soil release properties superior to conventional fabric treating processes; a fabric care composition that provides superior stain removal performance compared to conventional stain removal compositions.

#### Summary of the invention

The present invention meets and satisfies the needs identified above. The present invention relates to surface care compositions, preferably fabric care compositions, more preferably silicone- and starch-free fabric care compositions to be applied on a new and/or clean surfaces, preferably fabric surfaces, fully or in discrete regions thereof, comprising a film-forming polymer which provides superior soil removal performance without detracting from the particulate stain removal performance, as determined by the Test Protocol described hereinafter, treating processes employing such surface care compositions, preferably fabric care compositions to impart soil release properties to new and/or clean surfaces, preferably fabric surfaces.

It has now been discovered that an excellent soil removal performance can be achieved in a fabric treatment process whereby a new and/or clean fabric is treated fully or in discrete regions thereof, by a silicone- and starch-free fabric care composition comprising a polymer forming a film on the surface of the fabric and having a low affinity for the fabric surface. The film produced by the film-forming polymer of the present invention, is more easily removed in a subsequent conventional cleaning process. The fabric treating process of the present invention provides superior stain removal while not impacting the particulate stain removal performance of the fabric care composition.

Although the surface care compositions of the present invention are directed mainly to treating fabric surfaces, namely garments and clothing, other fabric surfaces such as carpets, upholstery. fabric curtains, fabric wall papers, fabric tablecloths, fabric napkins, fabric-covered furniture. bed linens, and non-fabric surfaces such as hardwood floors, tile floors, linoleum floors.

WO 00/65015 PCT/US00/11056

jewelry, wallpaper coverings can also be treated with the surface care compositions of the present invention under the methods of the present invention.

5

In one aspect of the present invention, a surface care composition, preferably a fabric care composition, more preferably a silicone- and starch-free fabric care composition comprising a film-forming polymer is provided.

In yet another aspect of the present invention, a fabric care composition, preferably a siliconeand starch-free fabric care composition comprising a film-forming polymer and a quaternary ammonium compound, preferably a biodegrabable quaternary ammonium compound is provided.

In still yet another aspect of the present invention, a method for treating a surface in need of treatment, preferably a fabric in need of treatment comprising contacting the surface, preferably the fabric surface with the surface care composition, preferably the fabric care composition, more preferably the silicone- and starch-free fabric care composition comprising a film-forming polymer of the present invention is provided.

In even still yet another aspect of the present invention, a method for treating a fabric in need of treatment comprising contacting the fabric with the fabric care composition, preferably the silicone- and starch-free fabric care composition comprising a film-forming polymer and a quaternary ammonium compound, preferably a biodegradable quaternary ammonium compound of the present invention is provided.

In still yet another aspect of the present invention, a method for protecting a surface against soiling, said method comprising the step of contacting said surface with a surface care composition comprising a film-forming polymer that forms a temporary film on said surface such that stains that come into contact with said temporary film can be removed from said surface upon washing.

In even still yet another aspect of the present invention, a method for protecting a fabric surface against soiling, said method comprising the step of contacting said fabric surface with a fabric care composition comprising a film-forming polymer that forms a temporary film on said fabric

surface such that stains that come into contact with said temporary film can be removed from said fabric surface upon washing.

In even still yet another aspect of the present invention, an article comprising the surface care composition, preferably the fabric care composition, more preferably the silicone- and starch-free fabric care composition of the present invention and instructions for using the surface care composition, preferably the fabric care composition, more preferably the silicon- and starch-free fabric care composition of the present invention to protect surfaces, preferably fabric surfaces from stains is provided.

Accordingly, the present invention provides a surface care composition, preferably a fabric care composition, more preferably a silicone- and starch-free fabric care composition and surface treating process, more preferably fabric surface treating process employing such composition that imparts to new and/or clean surfaces, preferably fabric surfaces superior soil/stain removal properties.

These and other aspects, objects, features and advantages will be clear from the following detailed description, examples and appended claims.

All percentages, ratios and proportions herein are on a weight basis unless otherwise indicated. All documents cited herein are hereby incorporated by reference.

### Detailed description of the invention

The fabric post-treatment compositions of the present invention comprises as an essential element a film-forming polymer and provide superior soil removal performance without detracting from the particulate stain removal performance.

### - Fabric Care Compositions

The fabric care compositions of the present invention comprise a film-forming polymer. Preferably, the fabric care compositions further comprise a quaternary ammonium compound.

It is desirable that the fabric care compositions of the present invention are free one or more of the following:

- i) resins;
- ii) silicone;
- compounds having a molecular weight of from 4,500 to 12,000 and selected from the group consisting of the ethylene oxide adducts of C<sub>12</sub> C<sub>18</sub> fatty alcohols, C<sub>12</sub> C<sub>18</sub> saturated fatty alcohols, and C<sub>14</sub> C<sub>18</sub> alkyl phenols;
- iv) quaternary ammonium compounds of the formula:

$$\begin{array}{ccc}
R^{2} \\
\downarrow_{\bigoplus} \\
R^{1} & N \longrightarrow R^{4}
\end{array}$$

wherein one or two of  $R^1$  -  $R^4$  are  $C_8$  -  $C_{25}$  alkyl groups or alkenyl groups and the others are  $C_1$  -  $C_3$  alkyl groups or hydroxyalkyl groups; and  $X^-$  is an anion group;

- v) nonionic surfactants having an HLB of 2-16;
- vi) ionic surfactants having a critical micelle concentration of less than 1.0 mmol;
- vii) water-soluble inorganic salts;
- viii) quaternary ammonium compounds of the formula:

$$R^{1} \xrightarrow{\stackrel{}{|_{\bigoplus}}} R^{4} \qquad X^{\bigoplus}$$

wherein  $R^1$  and  $R^2$  are  $C_{12}$  -  $C_{22}$  alkyl groups or alkenyl groups,  $R^8 \text{CONHC}_m H_{2m}$ ,  $R^9 \text{NHCOC}_m H_{2m}$ , or  $R^9 \text{OC}_m H_{2m}$  wherein  $R^8$  is  $C_{11}$  -  $C_{21}$  alkyl or alkenyl groups,  $R^9$  is  $C_{12}$  -  $C_{22}$  alkyl or alkenyl groups and m is 1-5;  $R^3$  and  $R^4$  are H,  $C_1$  -  $C_4$  alkyl groups or (CHY-CHZ<sub>p</sub>)OH where Y and Z are H or CH<sub>3</sub> provided that at least one of Y

or Z is H; and X<sup>-</sup> is H, CH<sub>3</sub>SO<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>SO<sub>4</sub>,  $\frac{1}{2}$  SO<sub>4</sub>, HCO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub> or HOCH<sub>2</sub>COO and p is 1-5;

ix) compounds of the formula:

$$\begin{array}{c|c}
R^{3} & & \\
N & \longrightarrow CH_{2} \\
\oplus & & \\
N & \longrightarrow CH_{2} \\
C_{n}H_{2n}QCR^{6} \\
\parallel & \\
O
\end{array}$$

wherein  $R^5$  and  $R^6$  are  $C_{11}$  -  $C_{21}$  alkyl groups or alkenyl groups,  $R^8COOC_mH_{2m}$ ,  $R^9OCOC_mH_{2m}$ ,  $R^8CONHC_mH_{2m}$ ,  $R^9NHCOC_mH_{2m}$  or  $R^9OC_mH_{2m}$  wherein  $R^8$  is  $C_{11}$  -  $C_{21}$  alkyl or alkenyl groups,  $R^9$  is  $C_{12}$  -  $C_{22}$  alkyl or alkenyl groups and m is 1-5;  $R^3$  is H,  $C_1$  -  $C_4$  alkyl groups or (CHY-CHZ<sub>p</sub>)OH where Y and Z are H or CH<sub>3</sub> provided that at least one of Y or Z is H; and X<sup>-</sup> is H, CH<sub>3</sub>SO<sub>4</sub>,  $C_2H_5SO_4$ ,  $\frac{1}{2}SO_4$ , HCO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub> or HOCH<sub>2</sub>COO and p is 1-5; Q is O or NH; and n is 1-3;

x) compounds of the formula:

wherein  $R^3$ ,  $R^4$  and  $R^7$  are H,  $C_1$  -  $C_4$  alkyl groups or (CHY-CHZ<sub>p</sub>)OH where Y and Z are H or CH<sub>3</sub> provided that at least one of Y or Z is H: and X<sup>-</sup> is H, CH<sub>3</sub>SO<sub>4</sub>,  $C_2$ H<sub>5</sub>SO<sub>4</sub>,  $V_2$  SO<sub>4</sub>, HCO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub> or HOCH<sub>2</sub>COO and p is 1-5;  $R^5$  and  $R^6$  are  $C_{11}$  -  $C_{21}$  alkyl groups or alkenyl groups,  $R^8$ COOC<sub>m</sub>H<sub>2m</sub>,  $R^9$ OCOC<sub>m</sub>H<sub>2m</sub>,  $R^8$ CONHC<sub>m</sub>H<sub>2m</sub>.  $R^9$ NHCOC<sub>m</sub>H<sub>2m</sub> or  $R^9$ OC<sub>m</sub>H<sub>2m</sub> wherein  $R^8$  is  $C_{11}$  -  $C_{21}$  alkyl or

xi)

alkenyl groups,  $R^9$  is  $C_{12}$  -  $C_{22}$  alkyl or alkenyl groups and m is 1-5;  $R^3$  is H,  $C_1$  -  $C_4$  alkyl groups or (CHY-CHZ<sub>p</sub>)OH where Y and Z are H or CH<sub>3</sub> provided that at least one of Y or Z is H; and X<sup>-</sup> is H, CH<sub>3</sub>SO<sub>4</sub>,  $C_2H_5SO_4$ ,  $V_2SO_4$ , HCO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub> or HOCH<sub>2</sub>COO and p is 1-5; compounds of the formula:

 $R^1$   $R^2$   $N-R^3$ 

wherein  $R^1$  and  $R^2$  are  $C_{12}$  -  $C_{22}$  alkyl groups or alkenyl groups,  $R^8CONHC_mH_{2m}$ ,  $R^9NHCOC_mH_{2m}$ , or  $R^9OC_mH_{2m}$  wherein  $R^8$  is  $C_{11}$  -  $C_{21}$  alkyl or alkenyl groups,  $R^9$  is  $C_{12}$  -  $C_{22}$  alkyl or alkenyl groups and m is 1-5;  $R^3$  and  $R^4$  are H,  $C_1$  -  $C_4$  alkyl groups or (CHY-CHZ<sub>p</sub>)OH where Y and Z are H or CH<sub>3</sub> provided that at least one of Y or Z is H; and X<sup>-</sup> is H, CH<sub>3</sub>SO<sub>4</sub>,  $C_2H_5SO_4$ , ½ SO<sub>4</sub>, HCO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub> or HOCH<sub>2</sub>COO and p is 1-5;

xii) compounds of the formula:

$$\begin{array}{c|c}
N & \longrightarrow CH_2 \\
N & \longrightarrow CH_2 \\
N & \longrightarrow CH_2 \\
C_nH_{2n}QCR^6 \\
0
\end{array}$$

wherein  $R^5$  and  $R^6$  are  $C_{11}$  -  $C_{21}$  alkyl groups or alkenyl groups,  $R^8COOC_mH_{2m}$ ,  $R^9OCOC_mH_{2m}$ ,  $R^8CONHC_mH_{2m}$ ,  $R^9NHCOC_mH_{2m}$  or  $R^9OC_mH_{2m}$  wherein  $R^8$  is  $C_{11}$  -  $C_{21}$  alkyl or alkenyl groups,  $R^9$  is  $C_{12}$  -  $C_{22}$  alkyl or alkenyl groups and m is 1-5;  $R^3$  is H,  $C_1$  -  $C_4$  alkyl groups or (CHY-CHZ<sub>p</sub>)OH where Y and Z are H or CH<sub>3</sub> provided that at least one of Y or Z is H; and X<sup>-</sup> is H, CH<sub>3</sub>SO<sub>4</sub>,  $C_2H_5SO_4$ ,  $C_2H_5SO_5$ ,  $C_2H_5SO_5$ ,  $C_2H_5SO_5$ ,  $C_2H_5SO_5$ ,  $C_2H_5$ ,

- xiii) water repellents;
- xiv) at least one of:
  - a) lipophilic surfactants having a HLB of 6 or less; and
  - b) propellants;
- xv) at least one of:
  - a) polymers or their salts prepared by polymerization of a monomer having at least a vinyl group and/or an aromatic ring, a sulfonic group and an average molecular weight of 10,000 to 500,000; and
  - b) carboxylic acid-containing polymers or salts thereof having recurring units of the formula [I]:

wherein X, Y and Z are each H, CH<sub>3</sub>, COOH or CH<sub>2</sub>COOH; and n is 10 to 2000; or of the formula [II]:

wherein m is 10-200;

- xv) swelling clay materials;
- xvi) alkalis;
- xvii) gelatinous materials;
- xviii) at least one of:
  - a) benzoic acid;

- b) fluroescent brightening agents; and
- c) perfumes;
- xix) starch and starch derivatives.

A more preferred fabric care composition in accordance with the present invention is a siliconeand starch-free fabric care composition comprising:

- a) from about 0.02% to about 5% of a film-forming polymer;
- b) from about 0.01% to about 5% of a quaternary ammonium compound;
- c) optionally, from about 0.01% to 80% adjunct materials; and
- d) balance solvent wherein said solvent is selected from the group consisting of water, alcohol, polyethylene glycol and mixtures thereof;

wherein said weight ratio of said film-forming polymer to quaternary ammonium compound is from about 50:1 to about 1:5.

The film-forming polymer of the present invention are preferably present in the fabric care compositions of the present invention at a level of from about 0.001% to about 20%, more preferably 0.02% to about 5%, most preferably from about 0.05% to about 2% by weight of the fabric care composition.

Quaternary ammonium compounds, preferably biodegradable quaternary ammonium compounds, when present in the fabric care compositions of the present invention, are preferably present at a level of from about 0.01% to about 5%, more preferably from about 0.01% to about 2% by weight of the fabric care composition.

Nonionic surfactants, preferably nonionic surfactants having an HLB value of from 8-14, when present in the fabric care compositions of the present invention are preferably present at a level of from about 0.01% to about 5%, more preferably from about 0.5% to about 2% by weight of the fabric care composition.

Perfumes, when present in the fabric care compositions of the present invention are preferably present at a level of from about 0.001% to about 1%, more preferably from about 0.1% to about 0.5% by weight of the fabric care composition.

...

When the fabric care composition of the present invention includes both a film-forming polymer and a quaternary ammonium compound, the film-forming polymer and quaternary ammonium compound are preferably present in a weight ratio of from about 50:1 to about 1:5, more preferably from about 10:1 to about 1:1.

In addition to the film-forming polymer, the fabric care composition of the present invention preferably includes one or more adjunct materials as fully described hereinafter, preferably one or more of the following quaternary ammonium compounds (preferably biodegradable quaternary ammonium compounds), nonionic surfactants having an HLB value of from 8-14, and perfumes. The precise nature of these adjunct materials, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

The preferred viscosity of the film-forming polymers in a 2% by weight aqueous solution is at least 5 Cp, more preferably at least 10 Cp.

The preferred level of fabric care composition applied to the surface of a fabric in need of treatment in accordance with the methods of the present invention is preferably from about 0.05 g/m<sup>2</sup> to about 10 g/m<sup>2</sup>, more preferably from about 0.1 g/m<sup>2</sup> to about 5 g/m<sup>2</sup>.

After the cleaning process the composition of the present invention is applied, preferably by spraying, on clean fabrics, in particular onto the problem areas where stains and soils may appear (collars, cuffs, sock heals, etc).

## Form of Fabric Care Composition

The fabric care compositions of the present invention can be in solid (powder, granules, bars. tablets), dimple tablets, liquid, paste, gel, spray, stick, or foam forms. Liquid, gel, spray, stick, foam, paste forms are preferred. Liquid and spray forms are highly preferred.

The liquid forms, can also be in a "concentrated" form which are diluted to form compositions with the usage concentrations, as given hereinbelow, for use in the "usage conditions". Concentrated compositions comprise a higher level of film-forming polymer, typically from about 1% to about 99%, preferably from about 2% to about 65%, more preferably from about 3% to about 25%, by weight of the concentrated fabric care composition. Concentrated compositions

are used in order to provide a less expensive product. When a concentrated product is used, i.e., when the film-forming polymer is from about 1% to about 99%, by weight of the concentrated composition, it is preferable to dilute the composition, preferably with water, before treating a fabric in need of treatment. Preferably, the water content of the "concentrated" form is less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

The present invention also relates to film-forming polymer-containing fabric care compositions incorporated into a spray dispenser to create an article of manufacture that can facilitate treatment of fabric articles and/or surfaces with said compositions containing the film-forming polymer and other optional ingredients at a level that is effective, yet is not discernible when dried on the surfaces. The spray dispenser comprises manually activated and non-manual powered (operated) spray means and a container containing the fabric care composition. The articles of manufacture preferably are in association with instructions for use to ensure that the consumer applies sufficient film-forming polymer to provide the desired benefit.

Preferably the articles of manufacture are in association with instructions for how to use the composition to treat fabrics correctly, to obtain the desirable fabric care results, for example, improved color appearance and/or pill prevention and/or abrasion resistance, while at the same time providing improved cleaning benefits, including, e.g., the manner and/or amount of composition to be used, and the preferred ways of stretching and/or smoothing, if any, the fabrics. It is important that the instructions be as simple and clear as possible. Accordingly, the use of pictures and/or icons to assist in explaining the instructions is desirable.

Liquid or solid, preferably powder, film-forming polymer-containing fabric care composition for treating fabric in accordance with the present invention comprise an effective amount of the film-forming polymer of the present invention, and optionally, fabric softener actives, perfume, electrolytes, chlorine scavenging agents, dye transfer inhibiting agents, dye fixative agents, phase stabilizers, chemical stabilizers including antioxidants, silicones, antimicrobial actives and/or preservatives, chelating agents, aminocarboxylate chelating agents, colorants, enzymes, brighteners, soil release agents, anti-encrustation agents, builders and/or mixtures thereof. Again, the composition is preferably packaged in association with instructions for use to ensure that the consumer knows what benefits can be achieved.

Yet another liquid or solid, preferably powder or granular, fabric care composition in accordance with the present invention comprises an effective amount of one or more Film-forming polymers, and optionally, surfactants, builders, perfume, chlorine scavenging agents, dye transfer inhibiting agents, dye fixative agents, dispersants, detergent enzymes, heavy metal chelating agents, suds suppressors, fabric softener actives, chemical stabilizers including antioxidants, silicones, antimicrobial actives and/or preservatives, soil suspending agents, soil release agents, optical brighteners, colorants, and the like, or mixtures thereof. Again, the composition is preferably packaged in association with instructions for use to ensure that the consumer knows what benefits can be achieved.

A preferred fabric care composition for treating fabric comprises an effective amount of one or more film-forming polymers, and optionally, perfume, fabric lubricants, adjunct fabric shape retention polymers, lithium salts, hydrophilic plasticizers, odor control agents, antimicrobial actives and/or preservatives, surfactants, enzymes, or mixtures thereof. Other optional ingredients can also be added, e.g., antioxidants, chelating agents, e.g., aminocarboxylate chelating agents, heavy metal chelating agents, antistatic agents, insect and moth repelling agents, dye transfer inhibiting agents, dye fixative agents, colorants, suds suppressors, and the like, and mixtures thereof. The composition is typically applied to fabric via a, e.g., dipping, soaking and/or spraying process followed by a drying step, including the process comprising a step of treating or spraying the fabric with the fabric care composition either outside or inside an automatic clothes dryer followed by, or concurrently with, the drying step in said clothes dryer. However, the composition may be applied by spraying the fabric with the fabric care composition prior to and/or during ironing, if needed. The application can be done industrially by large scale processes on textiles and/or finished garments and clothings, or in consumer's home by the use of commercial product.

The fabric care compositions herein can be made by any suitable process known in the art. Examples of such processes are described in U.S. Pat. No. 5,576,282.

The fabric care compositions of the present invention can be incorporated into a spray dispenser, or concentrated stick form that can create an article of manufacture that can facilitate the cleaning and/or fabric care or conditioning of fabric. If the spray treatment is a "pre-treat", which is followed by a wash cycle, then the spray treatment fabric care compositions preferably comprise

WO 00/65015 PCT/US00/11056

15

from about 0.01% to about 50% of film-forming polymer by weight the of total fabric care composition, more preferably from about 0.1% to about 3% of film-forming polymer by weight of the total fabric care composition. If the spray treatment compositions are desired to do the cleaning, as in the case of wash, then the spray treatment compositions preferably comprise from about 2 ppm to about 10000 ppm of the film-forming polymer by weight of the total fabric care composition, more preferably from about 200 ppm to about 5000 ppm of the film-forming polymer by weight of the total fabric care composition. In the latter case, a brief rinse, not a full wash cycle, is desirable after treatment. Such spray treatment compositions are typically packaged in a spray dispenser.

The spray-treatment compositions herein are typically packaged in spray dispensers. The spray dispensers can be any of the manually activated means for producing a spray of liquid droplets as is known in the art, e.g. trigger-type, pump-type, non-aerosol self-pressurized, and aerosol-type spray means. It is preferred that at least about 70%, more preferably, at least about 80%, most preferably at least about 90% of the droplets have a particle size of smaller than about 200 microns.

The spray dispenser can be an aerosol dispenser. Said aerosol dispenser comprises a container which can be constructed of any of the conventional materials employed in fabricating aerosol containers. The dispenser must be capable of withstanding internal pressure in the range of from about 20 to about 110 p.s.i.g., more preferably from about 20 to about 70 p.s.i.g. The one important requirement concerning the dispenser is that it be provided with a valve member which will permit the wrinkle reducing composition contained in the dispenser to be dispensed in the form of a spray of very fine, or finely divided, particles or droplets. The aerosol dispenser utilizes a pressurized sealed container from which the wrinkle reducing composition is dispensed through a special actuator/valve assembly under pressure. The aerosol dispenser is pressurized by incorporating therein a gaseous component generally known as a propellant. Common aerosol propellants, e.g., gaseous hydrocarbons such as isobutane, and mixed halogenated hydrocarbons. are not preferred. Halogenated hydrocarbon propellants such as chlorofluoro hydrocarbons have been alleged to contribute to environmental problems. Preferred propellants are compressed air. nitrogen, inert gases, carbon dioxide, etc. A more complete description of commercially available aerosol spray dispensers appears in U.S. Pat. Nos.: 3,436,772, Stebbins, issued Apr. 8. 1969; and 3,600,325, Kaufman et al., issued Aug. 17, 1971; both of said references are incorporated herein by reference.

7

Preferably the spray dispenser can be a self-pressurized non-aerosol container having a convoluted liner and an elastomeric sleeve. Said self-pressurized dispenser comprises a liner/sleeve assembly containing a thin, flexible radially expandable convoluted plastic liner of from about 0.010 to about 0.020 inch thick, inside an essentially cylindrical elastomeric sleeve. The liner/sleeve is capable of holding a substantial quantity of odor-absorbing fluid product and of causing said product to be dispensed. A more complete description of self-pressurized spray dispensers can be found in U.S. Pat. Nos.: 5,111,971, Winer, issued May 12, 1992; and 5,232,126, Winer, issued Aug. 3, 1993; both of said references are herein incorporated by reference. Another type of aerosol spray dispenser is one wherein a barrier separates the wrinkle reducing composition from the propellant (preferably compressed air or nitrogen), as is disclosed in U.S. Pat. No. 4,260,110, issued Apr. 7, 1981, incorporated herein by reference. Such a dispenser is available from EP Spray Systems, East Hanover, N.J.

More preferably, the spray dispenser is a non-aerosol, manually activated, pump-spray dispenser. Said pump-spray dispenser comprises a container and a pump mechanism which securely screws or snaps onto the container. The container comprises a vessel for containing the wrinkle reducing composition to be dispensed.

The pump mechanism comprises a pump chamber of substantially fixed, volume, having an opening at the inner end thereof. Within the pump chamber is located a pump stem having a piston on the end thereof disposed for reciprocal motion in the pump chamber. The pump stem has a passageway there through with a dispensing outlet at the outer end of the passageway and an axial inlet port located inwardly thereof.

The container and the pump mechanism can be constructed of any conventional material employed in fabricating pump-spray dispensers, including, but not limited to: polyethylene: polypropylene, polyethyleneterephthalate; blends of polyethylene, vinyl acetate, and rubber elastomer. Other materials can include stainless steel. A more complete disclosure of commercially available dispensing devices appears in: U.S. Pat. Nos.: 4,895,279, Schultz, issued Jan. 23, 1990; 4,735,347, Schultz et al., issued Apr. 5, 1988; and 4,274,560, Carter, issued Jun. 23, 1981; all of said references are herein incorporated by reference.

Most preferably, the spray dispenser is a manually activated trigger-spray dispenser. Said triggerspray dispenser comprises a container and a trigger both of which can be constructed of any of the conventional material employed in fabricating trigger-spray dispensers, including, but not limited to: polyethylene, polypropylene, polyacetal, polycarbonste, polyethylene-terephthalate, polyvinyl chloride, polystyrene, blends of polyethylene, vinyl acetate, and rubber elastomer. Other materials can include stainless steel and glass. The trigger-spray dispenser does not incorporate a propellant gas. The trigger-spray dispenser herein is typically one which acts upon a discrete amount of the wrinkle reducing composition itself, typically by means of a piston or a collapsing bellows that displaces the composition through a nozzle to create a spray of thin liquid. Said trigger-spray dispenser typically comprises a pump chamber having either a piston or bellows which is movable through a limited stroke response to the trigger for varying the volume of said pump chamber. This pump chamber or bellows chamber collects and holds the product for dispensing. The trigger spray dispenser typically has an outlet check valve for blocking communication and flow of fluid through the nozzle and is responsive to the pressure inside the chamber. For the piston type trigger sprayers, as the trigger is compressed, it acts on the fluid in the chamber and the spring, increasing the pressure on the fluid. For the bellows spray dispenser, as the bellows is compressed, the pressure increases on the fluid. The increase in fluid pressure in either trigger-spray dispenser acts to open the top outlet check valve. The top valve allows the product to be forced through the swirl chamber and out the nozzle to form a discharge pattern. An adjustable nozzle cap can be used to vary the pattern of the fluid dispensed.

For the piston spray dispenser, as the trigger is released, the spring acts on the piston to return to its original position. For the bellows spray dispenser, the bellows acts as the spring to return to its original position. This action causes a vacuum in the chamber. The responding fluid acts to close the outlet valve while opening the inlet valve drawing product up the chamber from the reservoir.

A more complete disclosure of commercially available dispensing devices appears in U.S. Pat. Nos.: 4,082,223, Nozawa, issued Apr. 4, 1978; 4,161,288, McKinney, issued Jul. 7, 1985; 4,434,917, Saito et al., issued Mar. 6, 1984; and 4,819,835, Tasaki, issued Apr. 11, 1989; 5,303,867, Peterson, issued Apr. 19, 1994; all of said references are incorporated herein by reference.

A broad array of trigger sprayers or finger pump sprayers are suitable for use with the compositions of this invention. These are readily available from suppliers such as Calmar, Inc., City of Industry, California; CSI (Continental Sprayers, Inc.), St. Peters, Missouri; Berry Plastics Corp., Evansville, Indiana - a distributor of Guala ® sprayers; or Seaquest Dispensing, Cary, Ill.

For smaller four fl-oz size (about 118 ml), a finger pump can be used with canister or cylindrical bottle. The preferred pump for this application is the cylindrical Euromist II® from Seaquest Dispensing.

It has been found that film-forming polymers impart to the fabric improved color appearance and/or pill prevention and/or abrasion resistance. These benefits provided by the film-forming polymer improve the appearance of the fabric.

#### Film-Forming Polymers

Film-forming polymers suitable for the fabric care compositions and treating processes of the present invention preferably have the following characteristics of film forming and of providing superior soil removal without detracting from the particulate stain removal performance of a subsequent cleaning process.

Nonlimiting examples of film-forming polymers include agar, algin, amylopectin, carboxymethylcellulose (CMC), dextrans, dextrins, ethylhydroxyethylcellulose (EHEC), guar, hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), hydroxybutylcellulose (HBC), karaya, larch, methylcellulose (MC), tamarind, scleroglucan, xanthan, carboxymethylhydroxyethylcellulose (CMHEC), methoxypropyl methyl cellulose (MPMC), hexylcarboxymethyl cellulose, C12 - C20 alkyl carboxymethylcellulose, methylhydroxyethylcellulose (MHEC), methylhydroxypropylcellulose (MHPC), hydroxyethylmethylcellulose (HEMC), hydroxypropylmethylcellulose (HPMC), hydroxybutylmethylcellulose (HBMC) and mixtures thereof.

A preferred film-forming polymer is a water-soluble cellulose derivative.

A more preferred film-forming polymer is selected from the group consisting of substituted  $\beta$ -1,4-glucans and derivatives thereof as represented by formula [I]:

wherein R is selected from H,  $C_vH_{2v+1}$  with v being 1-18,  $C_wH_{2w}OH$  with w being 1-18,  $CH_2OC(O)CH_3$ ,  $(CH_2)_xCOOCH_3$  with x being 1-10,  $CH_2COOM$  with M being Na or K, and wherein the degree of polymerization as represented by n is from 50 to 10,000. In the glucose unit, positions 2, 3, and/or 6 can be substituted independently by R, and in the end glucose units, positions 1 and/or 4 can also be substituted. The degree of substitution is preferably no more than 3, more preferably from about 0.5 to about 3.

Even more preferred film-forming polymers are the substituted  $\beta$ -1,4-glucans selected from the group consisting of carboxymethylcellulose, ethylhydroxyethylcellulose, hydroxyethylcellulose, hydroxybutylcellulose, methylcellulose, methoxypropyl methyl cellulose, carboxymethylhydroxyethylcellulose, hexylcarboxymethyl cellulose,  $C_{12}$  -  $C_{20}$  alkyl carboxymethylcellulose, methylhydroxyethylcellulose, methylhydroxypropylcellulose, hydroxyethylcellulose, hydroxybutylmethylcellulose and mixtures thereof.

Highly preferred film-forming polymers are selected from the group consisting of: hydroxypropylcellulose, hydroxypropylmethylcellulose, carboxymethylcellulose, hexylcarboxymethyl cellulose,  $C_{12}$  -  $C_{20}$  alkyl carboxymethylcellulose and mixtures thereof.

Examples of such film-forming polymers are commercially available from the following companies: Aqualon, Dow Chemical, ShimEtsu, MetsaSeila, Akzo Nobel, Zoltak, Nippon Soda, Sigma. In particular, Hydroxypropyl-cellulose (HPC): Klucel from Aqualon; Hydroxypropylmethylcellulose (HPMC): e.g. Metolose SH from ShinEtsu Chemical co, Ltd; Carboxymethylcellulose (CMC): Blanose from Aqualon; Methylcellulose (MC): e.g. Metolose

SM from ShinEtsu Chemical Co.,Ltd, Benecel from Aqualon; Methylhydroxyethylcellulose (HEMC): e.g. Metolose SE from Shin Etsu Chemical Co., Ltd; Hydroxyethylcellulose (HEC): Natrosol from Aqualon; Carbomethylhydroxyethylcellulose; Ethylhydroxyethylcellulose: Aqualon from Aqualon.

Without wishing to be bound by theory, it is believed that the selected polymer of the present invention demonstrate relatively low affinity to the fiber surface in a cleaning situation and low soil permeability properties. Moreover, it is believed that compounds with no or little film forming properties and high surface affinity show poor stain release and a negative for particulate stain removal.

The selected film-forming polymer of the present invention, upon naturally drying, tumble drying and/or ironing forms a protective film on the fiber surface that provides a barrier against stain and soil penetration into the fiber, incrustation, improves feel, helps ironing, and protects against wear and colour damage. During the subsequent cleaning process, e.g. wash cycle and/or dry cleaning, the polymeric film dissolves and loosens the soil/stain from the fabric fiber. Such polymeric film dissolution greatly facilitates the cleaning and provide superior cleaning.

### **Quaternary Ammonium Compounds**

Suitable quaternary ammonium compounds for use in the present invention include, but are not limited to, cationic surfactants, cationic softeners, biodegradable quaternary ammonium compounds and mixtures thereof. The preferred quaternary ammonium compounds for use in the fabric care compositions and methods of the present invention are biodegradable quaternary ammonium compounds.

<u>Cationic Surfactants</u> - Cationic detersive surfactants suitable for use in the compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula:

$$[R^2(OR^3)_y][R^4(OR^3)_y]_2R^5N+X-$$

wherein  $R^2$  is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each  $R^3$  is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)-.

CH<sub>2</sub>CH(CH<sub>2</sub>OH)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and mixtures thereof; each  $R^4$  is selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, benzyl ring structures formed by joining the two  $R^4$  groups, -CH<sub>2</sub>CHOH-CHOHCOR<sup>6</sup>CHOHCH<sub>2</sub>OH wherein  $R^6$  is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0;  $R^5$  is the same as  $R^4$  or is an alkyl chain wherein the total number of carbon atoms of  $R^2$  plus  $R^5$  is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):

Formula I

whereby R1 is a short chain length alkyl (C6-C10) or alkylamidoalkyl of the formula (II) :

Formula II

y is 2-4, preferably 3,

whereby R2 is H or a C1-C3 alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R3, R4 and R5 are either the same or different and can be either a short chain alkyl (C1-C3) or alkoxylated alkyl of the formula III,

whereby X is a counterion, preferably a halide, e.g. chloride or methylsulfate.

#### Formula III

R6 is  $C_1$ - $C_4$  and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined in formula I whereby  $R_1$  is  $C_8$ ,  $C_{10}$  or mixtures thereof, x=0,  $R_3$ ,  $R_4=CH_3$  and  $R_5=CH_2CH_2OH$ .

More preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula:

$$R_1R_2R_3R_4N^+X^-(i)$$

wherein  $R_1$  is  $C_8$ - $C_{16}$  alkyl, each of  $R_2$ ,  $R_3$  and  $R_4$  is independently  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxy alkyl, benzyl, and - $(C_2H_{40})_XH$  where x has a value from 2 to 5, and X is an anion. Not more than one of  $R_2$ ,  $R_3$  or  $R_4$  should be benzyl.

The preferred alkyl chain length for R<sub>1</sub> is C<sub>12</sub>-C<sub>15</sub> particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R<sub>2</sub>R<sub>3</sub> and R<sub>4</sub> are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are:

coconut trimethyl ammonium chloride or bromide; coconut methyl dihydroxyethyl ammonium chloride or bromide; decyl triethyl ammonium chloride; decyl dimethyl hydroxyethyl ammonium chloride or bromide; C<sub>12-15</sub> dimethyl hydroxyethyl ammonium chloride or bromide; coconut dimethyl hydroxyethyl ammonium chloride or bromide; myristyl trimethyl ammonium methyl sulphate; lauryl dimethyl benzyl ammonium chloride or bromide; lauryl dimethyl (ethenoxy)<sub>4</sub> ammonium chloride or bromide; choline esters (compounds of formula (i) wherein R<sub>1</sub> is

WO 00/65015 PCT/US00/11056

23

CH<sub>2</sub>-CH<sub>2</sub>-O-C-C<sub>12-14</sub> alkyl and R<sub>2</sub>R<sub>3</sub>R<sub>4</sub> are methyl).  $\parallel$  O

di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

<u>Cationic Softeners</u> - Typical cationic fabric softening components include the water-insoluble quaternary-ammonium fabric softening actives or their corresponding amine precursor, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate.

Preferred cationic softeners among these include the following:

- 1) ditallow dimethylammonium chloride (DTDMAC);
- 2) dihydrogenated tallow dimethylammonium chloride;
- 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 7) stearyl benzyl dimethylammonium chloride;
- 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 10) C<sub>12-14</sub> alkyl hydroxyethyl dimethylammonium chloride;
- 11) C<sub>12-18</sub> alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 13) di(tallowyl-oxy-ethyl) dimethylammonium chloride;
- 14) ditallow imidazolinium methylsulfate;
- 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable Quaternary Ammonium Compounds - Highly preferred quaternary ammonium compounds for use in the fabric care compositions and methods of the present invention are biodegradable quaternary ammonium compounds. Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain

ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The biodegradable quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below:

$$\begin{bmatrix} R^{3} & R^{2} \\ + & N - (CH_{2})_{n} - Q - T \end{bmatrix} X^{-1} \begin{bmatrix} R^{3} & R^{3} \\ + & N - (CH_{2})_{n} - CH - CH_{2} \\ R^{3} & Q & Q \\ & & 1 & 1/2 \end{bmatrix} X^{-1}$$
(II)

wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-,  $-NR^4-C(O)-$ ,  $-C(O)-NR^4-$ ;

 $R^1$  is  $(CH_2)_n$ -Q- $T^2$  or  $T^3$ ;

 $R^2$  is  $(CH_2)_m$ -Q- $T^4$  or  $T^5$  or  $R^3$ ;

 $R^3$  is  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  hydroxyalkyl or H;

 $R^4$  is H or  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  hydroxyalkyl;

 $T^1$ ,  $T^2$ ,  $T^3$ ,  $T^4$ ,  $T^5$  are independently  $C_{11}$ - $C_{22}$  alkyl or alkenyl;

n and m are integers from 1 to 4; and

X<sup>-</sup> is a softener-compatible anion.

Non-limiting examples of softener-compatible anions include chloride or methyl sulfate. The alkyl, or alkenyl, chain  $T^1$ ,  $T^2$ ,  $T^3$ ,  $T^4$ ,  $T^5$  must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched.

Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein  $T^1$ ,  $T^2$ ,  $T^3$ ,  $T^4$ ,  $T^5$  represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of biodegradable quaternary ammonium compounds suitable for use in the fabric care compositions and methods of the present invention include:

- 1) N.N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
- 3) N.N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
- 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
- 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride; and mixtures of any of the above materials.

#### **Test Protocol**

To determine whether a film-forming polymer can provide superior stain/soil removal performance without detracting from the particulate stain removal performance, such as clay stain removal performance, the following Test Protocols should be used.

# PROTOCOL SEBUM STAIN MAKING

Fabric: – Muslin cotton (197 g / m²)

Soil: - Sebum (ex WFK)

Synthetic pigment wfk-09V (ex WFK)

Soiling procedure – Weigh 8 g sebum

- Weigh 2 g pigment

Homogenize

 Apply soil with brush [ evenly and consistently from right to left and from left to right to cover a surface of 8 cm x 2 cm ]

- Ageing: Overnight line drying

# PROTOCOL CLAY STAIN MAKING

Fabric:

Muslin cotton (197 g / m²)

Soil:

Clay (preferably ex backyard P&G ETC - building)

Soiling procedure

- Weigh 2 g clay

- Add 10 ml industrial water

- Mix thoroughly via magnetic stirrer

 Put template on fabric ( rubber ring of ± 5 mm thick with inner diameter of 7 cm )

 Apply soil with brush [ evenly and consistently using clockwise and counterclockwise strokes to cover the template surface ]

- Ageing: Line dry stains overnight before first use

# PROTOCOL POLYMER PREPARATION

- Weigh polymer (e.g. 20 g for 1 liter)
- Put about 1 / 2 of the required volume as hot demineralized water ( above 70 ° C ) in a vessel
- Gradually add polymer while stirring
- Keep stirring until total amount is dispersed
- Add remainder of water as cold demineralized water while stirring to lower the temperature of the dispersion
- Place vessel in ice water to cool polymer solution down to 0 to 5 °C.
- Keep stirring till transparent solution.

# PROTOCOL SPRAYING PROCESS

- Fill small vial with polymer solution
- Open main air valve
- Open air valve of pressure regulator
- Set pressure on 2 bar
- Weigh fabric before spraying
- Spray solution on fabric ( distance vial fabric ± 20 cm ) e.g. target 2 g / m²
- Weigh fabric again
- Line dry fabric for several hours

# PROTOCOL WASHING TEST

Stains: Clay and artificial sebum on muslin cotton

Internal replicates: 4 / type of stain.

External replicates: 2

Wash conditions:

Miele W715

40 °C short cycle 30 g Ariel Futur

Brussels city water hardness

After washing and ironing, the stains are graded (visual grading - see protocol)

#### **PROTOCOL**

#### Reference Treatment

Washing of Sebum and Clay stained fabric without the fabric care treatment process (Polymer Preparation and Spraying Process steps).

**PROTOCOL** 

PSU - grading

PSU grading is a visual grading versus a reference treatment using the Scheffe scale from 0 to 4 with

SCORE	MEANING
0 1 2 3 4	There is no difference I think this one is better ( unsure ) I know this one is better (sure ) This one is a lot better This one is a whole lot better

#### **Adjunct Materials**

The fabric care compositions of the present invention comprise an effective amount of the film-forming polymer, and preferably one or more of the above-described preferred ingredients, and optionally one or more of the following conventional cleaning adjunct materials either to improve the performance of the film-forming polymer, e.g., in the areas of wrinkle control, anti-wear, soil release, tensile strength and the like, or to provide additional benefits, such as odor control, antimicrobial, and the like. The useful optional cleaning adjunct materials are those that are compatible with the film-forming polymer, in that they do not interfere and/or substantially or significantly diminish the benefits provided by the film-forming polymer. The precise nature of these optional cleaning adjunct materials, and levels of incorporation thereof will depend on the physical form of the fabric care compositions, and the nature of the cleaning operation for which it is to be used.

Examples of such cleaning adjunct materials include, but are not limited to, the following.

<u>Preservatives</u> - The fabric care compositions herein may also optionally contain one or more preservatives. The function of the preservatives is to prevent organisms/micro-organisms from breeding and growing on the fabrics treated with the laundry detergent and/or fabric care compositions herein. In the absence of such preservatives, organisms/micro-organisms could grow on the fabrics treated with the laundry detergent and/or fabric care compositions herein because a significant amount of carbohydrates/sugar could remain on the fabrics after treatment.

Sanitization of fabrics can be achieved by the compositions of the present invention containing antimicrobial materials, e.g., antibacterial halogenated compounds, quaternary compounds, and phenolic compounds.

It is preferable to use a broad spectrum preservative, e.g., one that is effective on both bacteria (both gram positive and gram negative) and fungi. A limited spectrum preservative, e.g., one that is only effective on a single group of microorganisms, e.g., fungi, can be used in combination with a broad spectrum preservative or other limited spectrum preservatives with complimentary and/or supplementary activity. A mixture of broad spectrum preservatives can also be used. In some cases where a specific group of microbial contaminants is problematic (such as Gram negatives), aminocarboxylate chelators may be used alone or as potentiators in conjunction with other preservatives. These chelators which include, e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof, can increase preservative effectiveness against Gram-negative bacteria, especially *Pseudomonas* species.

Antimicrobial preservatives useful in the present invention include biocidal compounds, i.e., substances that kill microorganisms, or biostatic compounds, i.e., substances that inhibit and/or regulate the growth of microorganisms.

### (1) Organic Sulfur Compounds

Preferred water-soluble preservatives for use in the present invention are organic sulfur compounds. Some non-limiting examples of organic sulfur compounds suitable for use in the present invention are:

#### (a) 3-Isothiazolone Compounds

A preferred preservative is an antimicrobial, organic preservative containing 3-isothiazolone groups having the formula:

wherein Y is an unsubstituted alkyl, alkenyl, or alkynyl group of from about 1 to about 18 carbon atoms, an unsubstituted or substituted cycloalkyl group having from about a 3 to about a 6 carbon ring and up to 12 carbon atoms, an unsubstituted or substituted aralkyl group of up to about 10 carbon atoms, or an unsubstituted or substituted aryl group of up to about 10 carbon atoms;  $R^1$  is hydrogen, halogen, or a  $(C_1-C_4)$  alkyl group; and  $R^2$  is hydrogen, halogen, or a  $(C_1-C_4)$  alkyl group.

Preferably, when Y is methyl or ethyl, R<sup>1</sup> and R<sup>2</sup> should not both be hydrogen. Salts of these compounds formed by reacting the compound with acids such as hydrochloric, nitric, sulfuric, etc. are also suitable.

This class of compounds is disclosed in U.S. Pat. No. 4,265,899, Lewis et al., issued May 5, 1981, and incorporated herein by reference. Examples of said compounds are: 5-chloro-2-methyl-4-isothiazolin-3-one; 2-n-butyl-3-isothiazolone; 2-benzyl-3-isothiazolone; 2-phenyl-3-isothiazolone, 2-methyl-4,5-dichloroisothiazolone;; 5-chloro-2-methyl-3-isothiazolone; 2-methyl-4-isothiazolin-3-one; and mixtures thereof. A preferred preservative is a water-soluble mixture of 5-chloro-2-methyl-4-isothiazolin-3-one, more preferably a mixture of about 77% 5-chloro-2-methyl-4-isothiazolin-3-one and about 23% 2-methyl-4-isothiazolin-3-one, a broad spectrum preservative available as a 1.5% aqueous solution under the trade name Kathon® CG by Rohm and Haas Company.

When Kathon® is used as the preservative in the present invention it is present at a level of from about 0.0001% to about 0.01%, preferably from about 0.0002% to about 0.005%, more preferably from about 0.0003% to about 0.003%, most preferably from about 0.0004% to about 0.002%, by weight of the composition.

Other isothiazolins include 1,2-benzisothiazolin-3-one, available under the trade name Proxel<sup>®</sup> products; and 2-methyl-4,5-trimethylene-4-isothiazolin-3-one, available under the trade name Promexal<sup>®</sup>. Both Proxel and Promexal are available from Zeneca. They have stability over a

wide pH range (i.e., 4-12). Neither contain active halogen and are not formaldehyde releasing preservatives. Both Proxel and Promexal are effective against typical Gram negative and positive bacteria, fungi and yeasts when used at a level from about 0.001% to about 0.5%, preferably from about 0.005% to about 0.05%, and most preferably from about 0.01% to about 0.02% by weight of the usage composition.

#### (b) Sodium Pyrithione

Another preferred organic sulfur preservative is sodium pyrithione, with water solubility of about 50%. When sodium pyrithione is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.01%, preferably from about 0.0002% to about 0.005%, more preferably from about 0.0003% to about 0.003%, by weight of the usage composition.

Mixtures of the preferred organic sulfur compounds can also be used as the preservative in the present invention.

#### (2) <u>Halogenated Compounds</u>

Preferred preservatives for use in the present invention are halogenated compounds. Some non-limiting examples of halogenated compounds suitable for use in the present invention are:

5-bromo-5-nitro-1,3-dioxane, available under the trade name Bronidox L® from Henkel. Bronidox L® has a solubility of about 0.46% in water. When Bronidox is used as the preservative in the present invention it is typically present at a level of from about 0.0005% to about 0.02%, preferably from about 0.001% to about 0.01%, by weight of the usage composition;

2-bromo-2-nitropropane-1,3-diol, available under the trade name Bronopol® from Inolex can be used as the preservative in the present invention. Bronopol has a solubility of about 25% in water. When Bronopol is used as the preservative in the present invention it is typically present at a level of from about 0.002% to about 0.1%, preferably from about 0.005% to about 0.05%, by weight of the usage composition;

- 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with acetic and gluconic acids can be used as a preservative in the present invention. The digluconate salt is highly water-soluble, about 70% in water, and the diacetate salt has a solubility of about 1.8% in water. When chlorohexidine is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.04%, preferably from about 0.0005% to about 0.01%, by weight of the usage composition.
- 1,1,1-Trichloro-2-methylpropan-2-ol, commonly known as chlorobutanol, with water solubility of about 0.8%; a typical effective level of chlorobutanol is from about 0.1% to about 0.5%, by weight of the usage composition.
- 4,4'- (Trimethylenedioxy)bis-(3-bromobenzamidine) dissethionate, or dibromopropamidine, with water solubility of about 50%; when dibromopropamidine is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.05%, preferably from about 0.0005% to about 0.01% by weight of the usage composition.

Mixtures of the preferred halogenated compounds can also be used as the preservative in the present invention.

#### (3) Cyclic Organic Nitrogen Compounds

Preferred water-soluble preservatives for use in the present invention are cyclic organic nitrogen compounds. Some non-limiting examples of cyclic organic nitrogen compounds suitable for use in the present invention are:

#### (a) Imidazolidinedione Compounds

Preferred preservatives for use in the present invention are imidazolidione compounds. Some non-limiting examples of imidazolidinedione compounds suitable for use in the present invention are:

1,3-bis(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione; commonly known as dimethyloldimethylhydantoin, or DMDM hydantoin, available as, e.g., Glydant® from Lonza. DMDM hydantoin has a water solubility of more than 50% in water, and is mainly effective on bacteria. When DMDM hydantoin is used, it is preferable that it be used in combination with a broad spectrum preservative such as Kathon CG®, or formaldehyde. A preferred mixture is about a 95:5 DMDM hydantoin to 3-butyl-2-iodopropynylcarbamate mixture, available under the trade name Glydant Plus® from Lonza. When Glydant Plus® is used as the preservative in the present invention, it is typically present at a level of from about 0.005% to about 0.2% by weight of the usage composition;

N-[1,3-bis(hydroxymethyl)2,5-dioxo-4-imidazolidinyl]-N,N'-bis(hydroxymethyl) urea, commonly known as diazolidinyl urea, available under the trade name Germall  $\Pi^{\otimes}$  from Sutton Laboratories, Inc. (Sutton) can be used as the preservative in the present invention. When Germall  $\Pi^{\otimes}$  is used as the preservative in the present invention, it is typically present at a level of from about 0.01% to about 0.1% by weight of the usage composition;

N,N"-methylenebis {N'-[1-(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl]urea}, commonly known as imidazolidinyl urea, available, e.g., under the trade name Abiol® from 3V-Sigma, Unicide U-13® from Induchem, Germall 115® from (Sutton) can be used as the preservative in the present invention. When imidazolidinyl urea is used as the preservative, it is typically present at a level of from about 0.05% to about 0.2%, by weight of the usage composition.

Mixtures of the preferred imidazolidinedione compounds can also be used as the preservative in the present invention.

#### (b) Polymethoxy Bicyclic Oxazolidine

Another preferred water-soluble cyclic organic nitrogen preservative is polymethoxy bicyclic oxazolidine, having the general formula:

$$CH_2OCH_2)OH$$

where n has a value of from about 0 to about 5, and is available under the trade name Nuosept® C from Hüls America. When Nuosept® C is used as the preservative, it is typically present at a level of from about 0.005% to about 0.1%, by weight of the usage composition.

Mixtures of the preferred cyclic organic nitrogen compounds can also be used as the preservative in the present invention.

#### (4) Low Molecular Weight Aldehydes

#### (a). Formaldehyde

A preferred preservative for use in the present invention is formaldehyde. Formaldehyde is a broad spectrum preservative which is normally available as formalin which is a 37% aqueous solution of formaldehyde. When formaldehyde is used as the preservative in the present invention, typical levels are from about 0.003% to about 0.2%, preferably from about 0.008% to about 0.1%. more preferably from about 0.01% to about 0.05%, by weight of the usage composition.

#### (b) Glutaraldehyde

A preferred preservative for use in the present invention is glutaraldehyde. Glutaraldehyde is a water-soluble, broad spectrum preservative commonly available as a 25% or a 50% solution in water. When glutaraldehyde is used as the preservative in the present invention it is typically present at a level of from about 0.005% to about 0.1%, preferably from about 0.01% to about 0.05%, by weight of the usage composition.

#### (5) Quaternary Compounds

Preferred preservatives for use in the present invention are cationic and/or quaternary compounds. Such compounds include polyaminopropyl biguanide, also known as polyhexamethylene biguanide having the general formula:

$$\label{eq:hcl-nh-cond} \begin{split} \text{HCl-NH}_2\text{-}(\text{CH}_2)_3\text{-}[\text{-}(\text{CH}_2)_3\text{-}\text{NH-C}(=\text{NH})\text{-}\text{NH-C}(=\text{NH-HCl})\text{-}\text{NH-}(\text{CH}_2)_3\text{-}]_x\text{-}(\text{CH}_2)_3\text{-}\text{NH-}\\ & \qquad \qquad \text{C(=NH)-NH-CN} \end{split}$$

Polyaminopropyl biguanide is a water-soluble, broad spectrum preservative which is available as a 20% aqueous solution available under the trade name Cosmocil CQ<sup>®</sup> from ICI Americas, Inc., or under the trade name Mikrokill<sup>®</sup> from Brooks; Inc.

1-(3-Chlorallyl) -3,5,7-triaza-1-azoniaadamantane chloride, available, e.g., under the trade name Dowicil 200 from Dow Chemical, is an effective quaternary ammonium preservative; it is freely soluble in water; however, it has the tendency to discolor (yellow), therefore it is not highly preferred.

Mixtures of the preferred quaternary ammonium compounds can also be used as the preservative in the present invention.

When quaternary ammonium compounds are used as the preservative in the present invention, they are typically present at a level of from about 0.005% to about 0.2%, preferably from about 0.01% to about 0.1%, by weight of the usage composition.

#### (6) <u>Dehydroacetic Acid</u>

A preferred preservative for use in the present invention is dehydroacetic acid. Dehydroacetic acid is a broad spectrum preservative preferably in the form of a sodium or a potassium salt so that it is water-soluble. This preservative acts more as a biostatic preservative than a biocidal preservative. When dehydroacetic acid is used as the preservative it is typically used at a level of from about 0.005% to about 0.2%, preferably from about 0.008% to about 0.1%, more preferably from about 0.01% to about 0.05%, by weight of the usage composition.

#### (7) Phenyl and Phenolic Compounds

Some non-limiting examples of phenyl and phenolic compounds suitable for use in the present invention are:

4,4'-diamidino- $\alpha,\omega$ -diphenoxypropane diisethionate, commonly known as propamidine isethionate, with water solubility of about 16%; and 4,4'-diamidino- $\alpha,\omega$ -diphenoxyhexane diisethionate, commonly known as hexamidine isethionate. Typical effective level of these salts is about 0.0002% to about 0.05% by weight of the usage composition.

Other examples are benzyl alcohol, with a water solubility of about 4%; 2-phenylethanol. with a water solubility of about 2%; and 2-phenoxyethanol, with a water solubility of about 2.67%; typical effective level of these phenyl and phenoxy alcohol is from about 0.1% to about 0.5%, by weight of the usage composition.

#### (8) Mixtures thereof

It is preferred that no, or essentially no, volatile low molecular weight monohydric alcohols such as ethanol and/or isopropanol are intentionally added to the composition of the present invention since these volatile organic compounds will contribute both to flammability problems and environmental pollution problems. If small amounts of low molecular weight monohydric alcohols are present in the composition of the present invention due to the addition of these alcohols to such things as perfumes and as stabilizers for some preservatives, it is preferable that the level of monohydric alcohol be less than about 5%, preferably less than about 3%, more preferably less than about 1%.

#### (9) Mixtures thereof

The preservatives of the present invention can be used in mixtures in order to control a broad range of microorganisms.

Bacteriostatic effects can sometimes be obtained for aqueous compositions by adjusting the composition pH to an acid pH, e.g., less than about pH 4, preferably less than about pH 3, or a basic pH, e.g., greater than about 10, preferably greater than about 11.

#### (10) Highly preferred preservatives

Highly preferred preservatives for use in the compositions of the present invention are selected from the group consisting of: isothiazolones; bronopol; hydantoins; oxazolidines; glutaraldehyde; isethionates; quats (benzalkoniums); and mixtures thereof.

<u>Perfumes</u> - The fabric care compositions of the present invention can further comprise a perfume component.

Fully-formulated fragrance can be prepared using numerous known odorant ingredients of natural or synthetic origin. The range of the natural raw substances can embrace not only readily-volatile, but also moderately-volatile and slightly-volatile components and that of the synthetics can include representatives from practically all classes of fragrant substances, as will be evident from the following illustrative compilation. In this list of perfume ingredients, some are commercial names conventionally known to one skilled in the art, and also includes isomers. Such isomers are also suitable for use in the present invention. A typical disclosure of suitable ketone and/or aldehydes, traditionally used in perfumery, can be found in "perfume and Flavor Chemicals", Vol. I and II, S. Arctander, Allured Publishing, 1994, ISBN 0-931710-35-5. Preferred for the purpose of the present invention are the aldehydes or ketones based products.

- Natural products such as tree moss absolute, basil oil, citrus fruit oils (such as bergamot oil, mandarin oil, etc.), mastix absolute, myrtle oil, palmarosa oil, patchouli oil, petitgrain oil Paraguay, wormwood oil;
- Alcohols such as farnesol, geraniol, linalool, nerol, phenylethyl alcohol, rhodinol, cinnamic alcohol;
- Aldehydes such as citral, Helional<sup>TM</sup>, alpha-hexyl-cinnamaldehyde, hydroxycitronellal, Lilial <sup>TM</sup> (p-tert.butyl-alpha -methyldihydrocinnamaldehyde), methylnonylacetaldehyde, 1-decanal. benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadienal: alpha-n-amyl cinnamic aldehyde, P.T. Bucinal, lyral, cymal, methyl nonyl acetaldehyde, hexanal. trans-2-hexenal, and mixture thereof;
- Ketones such as allylionone, alpha-ionone, beta -ionone, isoraldein (isomethyl- alpha -ionone). methylionone, Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-

Ionone, Iso-E-Super, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof;

- Esters such as allyl phenoxyacetate, benzyl salicylate, cinnamyl propionate, citronellyl acetate, citronellyl ethoxolate, decyl acetate, dimethylbenzylcarbinyl acetate, dimethylbenzylcarbinyl butyrate, ethyl acetoacetate, ethyl acetylacetate, hexenyl isobutyrate, linalyl acetate, methyl dihydrojasmonate, styrallyl acetate, vetiveryl acetate, etc.;
- Lactones such as gamma-undecalactone, various components often used in perfumery, such as musk ketone, indole, p-menthane-8-thiol-3-one, and methyl-eugenol;
- Acetals and ketals include the well-known methyl and ethyl acetals and ketals, as well as acetals or ketals based on benzaldehyde, those comprising phenylethyl moieties, or more recently developed specialties such as those described in a United States Patent entitled "Acetals and Ketals of Oxo-Tetralins and Oxo-Indanes, see U.S. Pat. No.
- 5,084,440, issued January 28, 1992, assigned to Givaudan Corp.;
- Recent synthetic specialties include the enol ethers of alkyl-substituted oxo-tetralins and oxo-indanes as described in U.S. Pat. 5,332,725, July 26, 1994, assigned to Givaudan; or Schiff Bases as described in U.S. Pat. 5,264,615, December 9, 1991, assigned to Givaudan;
- Perfume aldehyd and ketone amine addition products as described in pending patent application EP 98870227.0 and co-pending patent application EP 99870026.4, both in the name of Procter & Gamble Company.

Generally, when incorporated in the fabric post-treatment compositions of the present invention. the perfume will be comprised at a level of 0% to 10%, preferably 0% to 3%, more preferably 0% to 1% by weight of the total composition.

<u>Polysaccharides</u> - "Polysaccharides" herein is meant natural polysaccharides, and does not include polysaccharide derivatives or modified polysaccharides. Suitable polysaccharides for use in the treating compositions of the present invention include, but are not limited to, gums. arabinans, galactans, seeds and mixtures thereof.

Suitable polysaccharides that are useful in the present invention include polysaccharides with a degree of polymerization (DP) over 40, preferably from about 50 to about 100,000, more preferably from about 500 to about 50,000, constituting saccharides preferably include, but are not limited to, one or more of the following saccharides: isomaltose, isomaltotriose isomaltoteraose, isomaltotriose.

galactooligosaccharide, xylooligosaccharide, gentiooligosaccharides, disaccharides, glucose, fructose, galactose, xylose, mannose, arabinose, rhamnose, maltose, sucrose, lactose, maltulose, ribose, lyxose, allose, altrose, gulose, idose, talose, trehalose, nigerose, kojibiose, lactulose, oligosaccharides, maltooligosaccharides, trisaccharides, tetrasaccharides, pentasaccharides, hexasaccharides, oligosaccharides from partial hydrolysates of natural polysaccharide sources and mixtures thereof.

The polysaccharides can be extracted from plants, produced by organisms, such as bacteria, fungi, prokaryotes, eukaryotes, extracted from animals and/or humans. For example, xanthan gum can be produced by *Xanthomonas campestris*, gellan by *Sphingomonas paucimobilis*, xyloglucan can be extracted from tamarind seed.

The polysaccharides can be linear, or branched in a variety of ways, such as 1-2, 1-3, 104, 1-6, 2-3 and mixtures thereof.

It is desirable that the polysaccharides of the present invention have a molecular weight in the range of from about 10,000 to about 10,000,000, more preferably from about 50,000 to about 1,000,000, most preferably from about 50,000 to about 500,000.

Preferably, the polysaccharide is selected from the group consisting of: tamarind gum (preferably consisting of xyloglucan polymers), guar gum, locust bean gum (preferably consisting of galactomannan polymers), and other industrial gums and polymers, which include, but are not limited to, Tara, Fenugreek, Aloe, Chia, Flaxseed, Psyllium seed, quince seed, xanthan, gellan, welan, rhamsan, dextran, curdlan, pullulan, scleroglucan, chitin, hydroxyalkyl cellulose, arabinan (preferably from sugar beets), de-branched arabinan (preferably from sugar beets), arabinoxylan (preferably from rye and wheat flour), galactan (preferably from lupin and potatoes), pectic galactan (preferably from potatoes), galactomannan (preferably from carob, and including both low and high viscosities), glucomannan, lichenan (preferably from icelandic moss), mannan (preferably from ivory nuts), pachyman, rhamnogalacturonan, acacia gum, agar, alginates, chitosan, clavan, hyaluronic acid, heparin, inulin, cellodextrins, and mixtures thereof. These polysaccharides can also be treated (preferably enzymatically) so that the best fractions of the polysaccharides are isolated.

More preferred polysaccharides have a β-linked backbone.

Xyloglucan polymer is a highly preferred polysaccharide for use in the laundry and/or fabric care compositions of the present invention. Xyloglucan polymer is preferably obtained from tamarind seed polysaccharides. The preferred range of molecular weights for the xyloglucan polymer is from about 10,000 to about 1,000,000, more preferably from about 50,000 to about 200,000.

Polysaccharides, when present, are normally incorporated in the treating composition of the present invention at levels from about 0.1% to about 25%, preferably from about 0.2% to about 10% by weight of the treating composition.

Polysaccharides have a high affinity for binding with cellulose. Without wishing to be bound by theory, it is believed that the binding efficacy of the polysaccharides to cellulose depends on the type of linkage, extent of branching and molecular weight. The extent of binding also depends on the nature of the cellulose (i.e., the ratio of crystalline to amorphous regions in cotton, rayon, linen, etc.).

The natural polysaccharides can be modified with amines (primary, secondary, tertiary), amides, esters, ethers, alcohols, carboxylic acids, tosylates, sulfonates, nitrates, phosphates and mixtures thereof. Such a modification can take place in position 2, 3 and/or 6 of the glucose unit. Such modified or derivatized polysaccharides can be included in the compositions of the present invention in addition to the natural polysaccharides.

Nonlimiting examples of such modified polysaccharides include: carboxyl and hydroxymethyl substitutions (e.g., glucuronic acid instead of glucose); amino polysaccharides (amine substitution, e.g., glucosamine instead of glucose); C<sub>1</sub>-C<sub>6</sub> alkylated polysaccharides; acetylated polysaccharide ethers; polysaccharides having amino acid residues attached (small fragments of glycoprotein); polysaccharides containing silicone moieties. Suitable examples of such modified polysaccharides are commercially available from Carbomer and include, but are not limited to amino alginates, such as hexanediamine alginate, amine functionalized cellulose-like O-methyl-(N-1,12-dodecanediamine) cellulose, biotin heparin, carboxymethylated dextran, guar polycarboxylic acid, carboxymethylated locust bean gum, caroxymethylated xanthan, chitosan phosphate, chitosan phosphate sulfate, diethylaminoethyl dextran, dodecylamide alginate and mixtures thereof.

Oligosaccharides - The compositions of the present invention may include oligosaccharides. Suitable oligosaccharides that are useful in the present invention include oligosaccharides with a degree of polymerization (DP) of less than 20, preferably from about 1 to about 15, more preferably from about 2 to about 10, constituting monosaccharides preferably include, but are not limited to, one or more of the following monosaccharides: glucose, fructose, galactose, xylose, mannose, arabinose, rhamnose, ribose, lyxose, allose, altrose, gulose, idose, talose, and/or their derivatives. Preferred oligosaccharides have a molecular weight in the range of from about 300 to about 8000. Branched oligosaccharides are preferred over linear oligosaccharides.

Nonlimiting examples of suitable oligosaccharides can be obtained commercially from any of the suppliers - Carbomer (fructo-oligosaccharides, levo-oligosaccharides, inulin, dextra 5000, cellosaccharides, etc.,), Grain Processing Corporation (maltodextrin), Pharmacica Biotech (Dextran series), Palatinit (isomalt) and Showa Sangyo (Isomalto-500).

Oligosaccharides, when present, are normally incorporated in the cleaning composition at levels from about 1% to about 25%, preferably from about 2% to about 10% by weight of the laundry and/or fabric care composition.

<u>Surfactant System</u> - Detersive surfactants can be, and preferably are included in the fabric care compositions of the present invention. When present, surfactants comprise at least 0.01%, preferably at least about 0.1%, more preferably at least about 0.5%, most preferably at least about 0.5% to about 5% by weight of the fabric care composition.

The detersive surfactant can be nonionic, anionic, ampholytic, zwitterionic, cationic, semi-polar nonionic, and mixtures thereof, nonlimiting examples of which are disclosed in U.S. Patent Nos. 5,707,950 and 5,576,282. Preferred fabric care compositions comprise anionic detersive surfactants or mixtures of anionic surfactants with other surfactants, especially nonionic surfactants.

Anionic surfactants are highly preferred for use with the fabric care compositions of the present invention.

Nonlimiting examples of surfactants useful herein include the conventional  $C_{11}$ - $C_{18}$  alkyl benzene sulfonates and primary, secondary and random alkyl sulfates, the  $C_{10}$ - $C_{18}$  alkyl alkoxy sulfates, the  $C_{10}$ - $C_{18}$  alkyl polyglycosides and their corresponding sulfated polyglycosides,  $C_{12}$ - $C_{18}$  alpha-sulfonated fatty acid esters,  $C_{12}$ - $C_{18}$  alkyl and alkyl phenol alkoxylates

(especially ethoxylates and mixed ethoxy/propoxy),  $C_{12}$ - $C_{18}$  betaines and sulfobetaines ("sultaines"),  $C_{10}$ - $C_{18}$  amine oxides, and the like. Other conventional useful surfactants are listed in standard texts.

The surfactant is preferably formulated to be compatible with enzyme and bleaching components, if any, present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Nonionic Surfactants - Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. Commercially available nonionic surfactants of this type include Igepal<sup>TM</sup> CO-630, marketed by the GAF Corporation; and Triton<sup>TM</sup> X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkylphenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. Examples of commercially available nonionic surfactants of this type include Tergitol<sup>TM</sup> 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear alcohol with 9 moles ethylene oxide), Tergitol<sup>TM</sup> 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol<sup>TM</sup> 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene oxide), Neodol<sup>TM</sup> 23-3 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 3.0 moles of ethylene oxide), Neodol<sup>TM</sup> 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol<sup>TM</sup> 45-5 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, Kyro<sup>TM</sup> EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C12-C14 alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylPolysaccharides disclosed in U.S. Patent No. 4,565,647.

Preferred alkylpolyglycosides have the formula:  $R^2O(C_nH_{2n}O)_t(glycosyl)_x$ 

wherein R<sup>2</sup> is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. Examples of compounds of this type include certain of the commercially-available Plurafac<sup>TM</sup> LF404 and Pluronic<sup>TM</sup> surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic TM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylPolysaccharides, and mixtures thereof. Most preferred are  $C_8$ - $C_{14}$  alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and  $C_8$ - $C_{18}$  alcohol ethoxylates (preferably  $C_{10}$  avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula:  $R^2$  - C(O) -  $N(R^1)$  - Z wherein  $R^1$  is H, or  $R^1$  is  $C_{1-4}$  hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof,  $R^2$  is  $C_{5-31}$  hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably,  $R^1$  is methyl,  $R^2$  is a straight  $C_{11-15}$  alkyl or  $C_{16-18}$  alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Anionic Surfactants - Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:

wherein  $R^3$  is a  $C_8$ - $C_{20}$  hydrocarbyl, preferably an alkyl, or combination thereof,  $R^4$  is a  $C_1$ - $C_6$  hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably,  $R^3$  is  $C_{10}$ - $C_{16}$  alkyl, and  $R^4$  is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein  $R^3$  is  $C_{10}$ - $C_{16}$  alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO<sub>3</sub>M wherein R preferably is a  $C_{10}$ - $C_{24}$  hydrocarbyl, preferably an alkyl or hydroxyalkyl having a  $C_{10}$ - $C_{20}$  alkyl component, more preferably a  $C_{12}$ - $C_{18}$  alkyl or hydroxyalkyl, and M is H or a cation. Typically, alkyl chains of  $C_{12}$ - $C_{16}$  are preferred for lower wash temperatures (e.g. below about 50°C) and  $C_{16-18}$  alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for detersive purposes include salts of soap,  $C_8$ - $C_{22}$  primary of secondary alkanesulfonates,  $C_8$ - $C_{24}$  olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179,  $C_8$ - $C_{24}$  alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated  $C_{12}$ - $C_{18}$  monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated  $C_{6}$ - $C_{12}$  diesters), acyl sarcosinates, sulfates of alkylPolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula  $RO(CH_2CH_2O)_k$ - $CH_2COO$ -M+ wherein R is a  $C_8$ - $C_{22}$  alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such

as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929.678. issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Highly preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula  $RO(A)_mSO3M$  wherein R is an unsubstituted  $C_{10}$ -C24 alkyl or hydroxyalkyl group having a C10-C24 alkyl component, preferably a C12-C20 alkyl or hydroxyalkyl, more preferably C12-C18 alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium. potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethylammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (1.0) sulfate  $(C_{12}-C_{18}E(1.0)M)$ ,  $C_{12}-C_{18}$  alkyl polyethoxylate (2.25) sulfate  $(C_{12}-C_{18}E(2.25)M)$ ,  $C_{12}-C_{18}$  alkyl polyethoxylate (3.0) sulfate  $(C_{12}-C_{18}E(3.0)M)$ , and C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (4.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(4.0)M), wherein M is conveniently selected from sodium and potassium.

When included therein, the fabric care compositions of the present invention typically comprise from about 1%, preferably from about 3% to about 40%, preferably about 20% by weight of such anionic surfactants.

Ampholytic Surfactants - Ampholytic surfactants, examples of which are described in U.S. Patent No. 3,929,678, are also suitable for use in the fabric care compositions of the present invention.

When included therein, the fabric care compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 15%, preferably to about 10% by weight of such ampholytic surfactants.

Zwitterionic Surfactants - Zwitterionic surfactants, examples of which are described in U.S. Patent No. 3,929,678, are also suitable for use in the fabric care compositions of the present invention.

When included therein, the fabric care compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 15%, preferably to about 10% by weight of such zwitterionic surfactants.

<u>Semi-polar Nonionic Surfactants</u> - Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides having the formula:

o

个

# $R^{3}(OR^{4})_{x}N(R^{5})_{2}$

wherein R<sup>3</sup> is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R<sup>4</sup> is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R<sup>5</sup> is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups (the R<sup>5</sup> groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure); water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

The amine oxide surfactants in particular include  $C_{10}$ - $C_{18}$  alkyl dimethyl amine oxides and  $C_8$ - $C_{12}$  alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the fabric care compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 15%, preferably to about 10% by weight of such semi-polar nonionic surfactants.

Cosurfactants - The fabric care compositions of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines. Suitable primary amines for use herein include amines according to the formula  $R_1NH_2$  wherein  $R_1$  is a  $C_6$ - $C_{12}$ , preferably  $C_6$ - $C_{10}$  alkyl chain or  $R_4X(CH_2)_n$ , X is -O-,-C(O)NH- or -NH-,  $R_4$  is a  $C_6$ - $C_{12}$  alkyl chain n is between 1 to 5, preferably 3.  $R_1$  alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C8-C10 oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido

propylamine. The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

LFNIs - Low foaming nonionic surfactants (LFNI) which are described in U.S. Patent Nos. 5,705,464 and 5,710,115 can be included in the fabric care compositions of the present invention. LFNI may be present in amounts from 0.01% to about 10% by weight, preferably from about 0.1% to about 10%, and most preferably from about 0.25% to about 4%. LFNIs are most typically used in automatic dishwashing detergent compositions (ADDs) on account of the improved water-sheeting action (especially from glass) which they confer to the ADD product. They also encompass non-silicone, nonphosphate polymeric materials further illustrated hereinafter which are known to defoam food soils encountered in automatic dishwashing.

Preferred LFNIs include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohols, and blends thereof with more sophisticated surfactants, such as the polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers as described in U.S. Patent Nos. 5,705,464 and 5,710,115.

LFNIs which may also be used include those POLY-TERGENT® SLF-18 nonionic surfactants from Olin Corp., and any biodegradable LFNI having the melting point properties discussed hereinabove.

These and other nonionic surfactants are well known in the art, being described in more detail in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detersive Systems", incorporated by reference herein.

<u>Dispersants</u> - One or more suitable polyalkyleneimine dispersants may be incorporated into the fabric care compositions of the present invention. Examples of such suitable dispersants can be found in European Patent Application Nos. 111,965, 111,984, and 112,592; U.S. Patent Nos. 4,597,898, 4,548,744, and 5,565,145. However, any suitable clay/soil dispersent or anti-redeposition agent can be used in the fabric care compositions of the present invention.

In addition, polymeric dispersing agents which include polymeric polycarboxylates and polyethylene glycols, are suitable for use in the present invention. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. Particularly suitable polymeric polycarboxylates can be derived

from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in U.S. 3,308,067.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000. most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000 preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Soil Release Agents - The fabric care compositions according to the present invention, to the extent that such soil release agents have not been previously discussed above as film-forming

agents, may optionally comprise one or more soil release agents. If utilized, soil release agents will generally comprise from about 0.01%, preferably from about 0.1%, more preferably from about 0.2% to about 5%, preferably to about 2% by weight, of the composition. Nonlimiting examples of suitable soil release polymers are disclosed in: U.S. Patent Nos. 5,728,671; 5,691,298; 5,599,782; 5,415,807; 5,182,043; 4,956,447; 4,976,879; 4,968,451; 4,925,577; 4,861,512; 4,877,896; 4,771,730; 4,711,730; 4,721,580; 4,000,093; 3,959,230; and 3,893,929; and European Patent Application 0 219 048.

Further suitable soil release agents are described in U.S. Patent Nos. 4,201,824; 4,240,918; 4,525,524; 4,579,681; 4,220,918; and 4,787,989; EP 279,134 A; EP 457,205 A; and DE 2,335,044.

Chelating Agents - The fabric care compositions of the present invention herein may also optionally contain a chelating agent which serves to chelate metal ions and metal impurities which would otherwise tend to deactivate the bleaching agent(s). Useful chelating agents can include amino carboxylates, phosphonates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof. Further examples of suitable chelating agents and levels of use are described in U.S. Pat. Nos. 5,705,464, 5,710,115, 5,728,671 and 5,576,282.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.01% to about 2%, more preferably from about 0.1% to about 1% by weight of the fabric care compositions herein.

Hydrogen Bond Breaking Agents - Suitable hydrogen bond breaking agents including, but not limited to, plant expansin and urea can optionally be incorporated into the fabric care compositions of the present invention.

pH and Buffering Variation - Many of the fabric care compositions described herein will be buffered, i.e., they are relatively resistant to pH drop in the presence of acidic soils. However, other compositions herein may have exceptionally low buffering capacity, or may be substantially unbuffered. Techniques for controlling or varying pH at recommended usage levels more

generally include the use of not only buffers, but also additional alkalis, acids, pH-jump systems, dual compartment containers, etc., and are well known to those skilled in the art.

Other Materials - Other cleaning adjunct materials optionally included in the treating compositions of the present invention can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or designed to improve the aesthetics of the compositions. Adjuncts which can also be included in compositions of the present invention, at their conventional art-established levels for use (generally, adjunct materials comprise, in total, from about 30% to about 99.9%, preferably from about 70% to about 95%, by weight of the compositions), include other active ingredients such as clay soil removal/antiredeposition agents, brighteners, dyes, perfumes, structure elasticizing agents, carriers, hydrotropes, processing aids, fillers, germicides, alkalinity sources, solubilizing agents and/or pigments. Suitable examples of such other cleaning adjunct materials and levels of use are found in U.S. Patent Nos. 5,576,282, 5,705,464, 5,710,115, 5,698,504, 5,695,679, 5,686,014 and 5,646,101.

#### Methods of Treating

Fabrics can be treated with the film-forming polymer-containing fabric care compositions by any method known in the art that accomplishes contacting the fabric with the film-forming polymer-containing fabric care composition.

A preferred embodiment of the present invention is a method for treating a fabric in need of treatment, wherein the method comprises contacting the fabric with an effective amount of film-forming polymer-containing fabric care composition such that the fabric care composition treats the fabric.

Other suitable methods include, but are not limited to, soaking the fabric in a solution containing the film-forming polymer-containing fabric care composition; spraying the fabric with a solution containing the film-forming polymer-containing fabric care composition; rubbing the fabric with a solid containing the film-forming polymer-containing fabric care composition; dipping the fabric in a solution containing the film-forming polymer-containing fabric care composition; rolling the film-forming polymer-containing fabric care composition onto the fabric, spreading the film-forming polymer-containing fabric care composition onto the fabric and brushing the film-forming polymer-containing fabric care composition onto the fabric.

Such methods can be used in industrial applications, such as in the textile industry, or in residential (domestic) applications, preferably, the methods are used in the residential (domestic) applications.

Further, these methods can be used independently of one another, or can be combined, concurrently or sequentially.

The use of the fabric care compositions of the present invention in accordance with these methods maintains the color appearance and/or pill prevention and/or abrasion resistance of a fabric in need of treatment through multiple wash cycles.

#### Product/Instructions

The present invention also encompasses the inclusion of instructions on the use of the film-forming polymer-containing fabric care compositions with the packages containing the fabric care compositions herein or with other forms of advertising associated with the sale or use of the fabric care compositions. The instructions may be included in any manner typically used by consumer product manufacturing or supply companies. Examples include providing instructions on a label attached to the container holding the composition; on a sheet either attached to the container or accompanying it when purchased; or in advertisements, demonstrations, and/or other written or oral instructions which may be connected to the purchase of the fabric care compositions.

The instructions, for instance, may include information relating to the temperature of the wash water; washing time; recommended settings on the washing machine; recommended amount of the fabric care composition to use; pre-soaking procedures; and spray-treatment procedures.

A product comprising a film-forming polymer-containing fabric care composition, the product further including instructions for using the fabric care composition to treat a fabric in need of treatment, the instructions including the step of: contacting said fabric with an effective amount of said fabric care composition for an effective amount of time such that said composition treats said fabric.

The product may be contained in a spray dispenser.

An article of commerce comprising a container containing a silicone- and starch-free fabric care composition comprising a film-forming polymer, which forms a temporary film on fabrics such that stains that come into contact with said temporary film can be removed from said fabric upon washing; wherein said container includes instructions for protecting fabrics from stains comprising the instruction to apply said fabric care composition to the surface of a fabric in need of treatment. Preferably, the fabric care composition of the present invention is applied to a fabric in need of treatment in a post-cleaning treatment process.

#### Examples

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention. In the fabric care compositions, any enzyme levels are expressed by percent of pure enzyme by weight of the total composition and unless otherwise specified, the adjunct materials are expressed as percent of cleaning adjunct materials by weight of the total compositions.

Further, in the following examples some abbreviations known to those of ordinary skill in the art are used, consistent with the disclosure set forth herein, and/or as defined herein below.

DEQA : Di-(tallowyl-oxy-ethyl) dimethyl ammonium chloride

DOEQA : Di-(oleyloxyethyl) dimethyl ammonium methylsulfate

DTDMAC : Ditallow dimethylammonium chloride

CTMAC : coconut trimethyl ammonium chloride

DMHELAC : dimethyl hydroxyethyl lauryl ammonium chloride

pKa of hydroxyl proton = 12.7

DAHEAMS : NN-di(alkoyl -oxy-ethyl)-N-methyl, N-(2-hydroxyethyl).

ammonium methyl sulfate with C16-C18 chain length

QAS  $R_2.N+(CH_3)_2(C_2H_4OH)$  with  $R_2 = C_{12}-C_{14}$ .

QAS 1 :  $R_2.N+(CH_3)_2(C_2H_4OH)$  with  $R_2 = C_8-C_{11}$ .

CXYEZ : A C<sub>1X</sub> - C<sub>1Y</sub> predominantly linear primary alcohol

condensed with an average of Z moles of ethylene oxide

Neodol 45-13 : C14-C15 linear primary alcohol ethoxylate, sold by Shell

Chemical CO.

Photoactivated Bleach : Sulfonated zinc phtalocyanine encapsulated in dextrin

soluble polymer.

Photoactivated Bleach 1 : Sulfonated alumino phtalocyanine encapsulated in dextrin

soluble polymer.

CMC : Sodium carboxymethyl cellulose.

HEC : Hydroxyethylcellulose HPC : Hydroxypropylcellulose

HBMC : Hydroxybutylmethylcellulose
MHPC : Methylhydroxypropylcellulose
MHEC : Methylhydroxyethylcellulose

MC : Methylcellulose

Brightener 1 : Disodium 4,4'-bis(2-sulphostyryl)biphenyl.

Brightener 2 : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)

stilbene-2:2'-disulfonate.

PEG: Polyethylene glycol, of a molecular weight of 400-30.000.

Alcohol : Ethanol, methanol, propanol,...

#	1	2	3	4	<u>5</u>
MC (Culminal MC12000)	1	1	2	3	5
SOLVENT					
Water	98			up to 100	
Alcohol		95			94
PEG			93		
QUATERNARY					
AMMONIUM				· ·	
COMPOUNDS					
DMHELAC		2	0.8		
DTDMAC				0.75	
PERFUME			0.1	0.001	
PHOTOBLEACH (in ppm				1ppm	
)					
BRIGHTENER			0.1		
PRESERVATIVES			2	0.25	
SURFACTANT		2			1
MINORS	1		2		

<u>#</u>	<u>6</u>	7	8	2	<u>10</u>	11
MHEC						
Culminal MHEC 6000	1	0.5		2		
PR						
Culminal MHEC			2			3
15000 PPF	•					
Culminal MHEC		1			2.5	
40000 PI					,	
SOLVENT						
WATER		up to			72	up to
		100				100
ALCOHOL	98.5		up to			67

			100	<del></del>	1	
			100			
PEG				95.4	25	
QUATERNARY						
AMMONIUM						
COMPOUNDS						
DMHELAC	,			2		
DPHEAC						1
DEQA					0.2	
DTDMAC			3			
PERFUME		,		0.5	0.3	
PHOTOBLEACH			1 ppm			l ppm
BRIGHTENER				0.1		
PRESERVATIVES	0.5	0.0001				
SURFACTANT						3
MINORS			2			0.5

<u>#</u>	12	13	14	<u>15</u>	<u>16</u>	<u>17</u>
МНРС						
Culminal MHPC	1		1			5
20000P		İ				
MHPC 22k ( SIGMA )				0.1		
METHOCEL K15M		1	1		0.5	
SOLVENT						
WATER	up to		75			88
+	100		•			
ALCOHOL		up to	21		91.2	
		100				
PEG				up to		5
				100	_	
QUATERNARY						
AMMONIUM						
COMPOUNDS						
DMHELAC					5	
DPHEAC			0.5			
DEQA				0.2		1
DTDMAC			1			
PERFUME		0.1			0.3	
PHOTOBLEACH		1 ppm		1 ppm		
PRESERVATIVES	0.001				0.5	
SURFACTANT		1	0.5	1	2	<u> </u>
MINORS	2					1

<u>#</u>	18	19	20	21	22	23	24	25	26
нрс		-			1	<del> </del>	#-	┼╼	<del>  -</del>
Aldrich HPC 370k	1	<del> </del>	1	<del> </del>	5				2
Aqualon Klucel M		2	+	<del> </del> -	<del>                                     </del>		<del> </del>	4	<del> </del>
Aqualon Klucel H				<del>                                     </del>	<del> </del>	2	5		<del> </del>
Nippon Soda HPC M	<del> </del>	1.	1	2	<u> </u>		+	+	
SOLVENT			<del> </del>	<del>                                     </del>	-	+	-	<del> </del>	
WATER	98		up to	<del> </del>	94	up to	90		32
			100			100			
ALCOHOL		43				70		95.4	32
PEG		50		97		<del> </del>	<del>                                     </del>		32
QUATERNARY	<del></del>	<del> </del>	1				-		
AMMONIUM									
COMPOUNDS									
DMHELAC			2			2			
DPHEAC	· · · · · ·	4	<b> </b>		1				
DEQA	0.2			1			2		
DTDMAC									2
PERFUME		0.5	0.5				0.5	0.5	
PHOTOBLEACH			1			1			
			ppm			ppm			
BRIGHTENER			0.001			0.001			
PRESERVATIVES		0.5				0.02		0.1	<u>-</u>
									. [
SURFACTANT	0.8		5			1	2.5	<del></del>	
MINORS			0.5						-

	27	28	29	30	31	32
HEC						
Aldrich HEC 90 k	2			5	1	
Aldrich HEC 1300 k		1			<del>                                     </del>	4
Hercules Natrosol 250			3	<del></del>	<del> </del>	
MR						
SOLVENT					1	
WATER	92.9			80	97	
ALCOHOL		up to	69.3		<del> </del>	
		100				
PEG			25	11		up to 100
QUATERNARY						
AMMONIUM						
COMPOUNDS				,		
DMHELAC					1	
DPHEAC	5		2			
DEQA	٠.			1		0.2
DTDMAC	·	2			-	
PERFUME			0.2		0.5	
PHOTOBLEACH		l ppm		<del></del>		1 ppm
BRIGHTENER		0.1				<del> </del>
PRESERVATIVES	0.1				0.5	0.001
SURFACTANT	90			3		0.8
MINORS			0.5			<del>                                     </del>

	<u>33</u>	34	35	36	37	38
CMC						
CMC (MW 100 - 150k)	2		5	4		
CMC ( MW 300 - 400 k		1	<del>                                     </del>		1	4
)					1	
SOLVENT		<del>                                     </del>	1			<del> </del>
WATER	95.8		<del>                                     </del>	80.9	97	up to 100
ALCOHOL		up to	up to	13		
		100	100			
PEG						
QUATERNARY	· · · · · · · · · · · · · · · · · · ·		<del> </del>			
AMMONIUM						
COMPOUNDS						
DMHELAC			<del> </del>		2	
DPHEAC	2					<del></del>
DEQA			0.2	0.1		<del></del>
DTDMAC		1	<del> </del>		<del></del>	0.2
PERFUME		<del></del>		1		0.05
PHOTOBLEACH		1 ppm				1 ppm
BRIGHTENER		0.001				0.1
PRESERVATIVES	0.2	,	0.001			0.001
SURFACTANT			2	1		0.8
MINORS			0.5			

	<u>39</u>	40	41
Hydroxybutylmethylcellulos	1	5	2
e	5	ļ	
SOLVENT			
Water	97		up to 100
Alcohol		up to 100	
PEG			10

QUATERNARY			
AMMONIUM			
COMPOUNDS			
DMHELAC			0.8
DEQA	· ·	0.2	
PERFUME			0.2
PHOTOBLEACH (in ppm)	f		l ppm
PRESERVATIVES		0.001	0.5
SURFACTANT			
MINORS	2		

Having described the invention in detail with reference to preferred embodiments and the examples, it will be clear to those skilled in the art that various changes and modifications may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

#### **EPO STYLE CLAIMS FOR 7535**

- 1. A fabric care composition comprising:
  - a) a film-forming polymer;

5 provided that said composition is free of:

- i) resins;
- ii) silicone;
- iii) compounds having a molecular weight of from 4,500 to 12,000 and selected from the group consisting of the ethylene oxide adducts of C<sub>12</sub> C<sub>18</sub> fatty alcohols, C<sub>12</sub> C<sub>18</sub> saturated fatty alcohols, and C<sub>14</sub> C<sub>18</sub> alkyl phenols;
- iv) quaternary ammonium compounds of the formula:

$$\begin{array}{ccc}
R^{2} \\
\downarrow \bigoplus \\
R^{1} & N \longrightarrow R^{4}
\end{array}$$

$$\begin{array}{ccc}
R^{2} \\
\downarrow \bigoplus \\
R^{3}
\end{array}$$

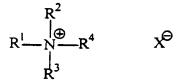
15

20

10

wherein one or two of  $R^1$  -  $R^4$  are  $C_8$  -  $C_{25}$  alkyl groups or alkenyl groups and the others are  $C_1$  -  $C_3$  alkyl groups or hydroxyalkyl groups; and  $X^-$  is an anion group;

- v) nonionic surfactants having an HLB of 2-16;
- vi) ionic surfactants having a critical micelle concentration of less than 1.0 mmol;
- vii) water-soluble inorganic salts;
- viii) quaternary ammonium compounds of the formula:



25

wherein  $R^1$  and  $R^2$  are  $C_{12}$  -  $C_{22}$  alkyl groups or alkenyl groups,  $R^8 \text{CONHC}_m H_{2m}$ ,  $R^9 \text{NHCOC}_m H_{2m}$ , or  $R^9 \text{OC}_m H_{2m}$  wherein  $R^8$  is  $C_{11}$  -  $C_{21}$  alkyl or alkenyl groups,  $R^9$  is  $C_{12}$  -  $C_{22}$  alkyl or alkenyl groups and m is 1-5;  $R^3$  and  $R^4$  are H,  $C_1$  -  $C_4$  alkyl groups or (CHY-CHZ<sub>p</sub>)OH where Y and Z are H or CH<sub>3</sub> provided that at least one of Y

or Z is H; and  $X^-$  is H, CH<sub>3</sub>SO<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>SO<sub>4</sub>, ½ SO<sub>4</sub>, HCO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub> or HOCH<sub>2</sub>COO and p is 1-5;

ix) compounds of the formula:

$$R^{5}$$
 $C$ 
 $\Theta$ 
 $CH_{2}$ 
 $CH_{2}$ 
 $C_{n}H_{2n}QCR^{6}$ 
 $C$ 
 $O$ 

5

wherein  $R^5$  and  $R^6$  are  $C_{11}$  -  $C_{21}$  alkyl groups or alkenyl groups,  $R^8COOC_mH_{2m}$ ,  $R^9OCOC_mH_{2m}$ ,  $R^8CONHC_mH_{2m}$ ,  $R^9NHCOC_mH_{2m}$  or  $R^9OC_mH_{2m}$  wherein  $R^8$  is  $C_{11}$  -  $C_{21}$  alkyl or alkenyl groups,  $R^9$  is  $C_{12}$  -  $C_{22}$  alkyl or alkenyl groups and m is 1-5;  $R^3$  is H,  $C_1$  -  $C_4$  alkyl groups or (CHY-CHZ<sub>p</sub>)OH where Y and Z are H or CH<sub>3</sub> provided that at least one of Y or Z is H; and X<sup>-</sup> is H, CH<sub>3</sub>SO<sub>4</sub>,  $C_2H_5SO_4$ ,  $\frac{1}{2}SO_4$ , HCO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub> or HOCH<sub>2</sub>COO and p is 1-5; Q is O or NH; and n is 1-3;

10

x) compounds of the formula:

15

20

wherein  $R^3$ ,  $R^4$  and  $R^7$  are H,  $C_1$  -  $C_4$  alkyl groups or  $(CHY-CHZ_p)OH$  where Y and Z are H or  $CH_3$  provided that at least one of Y or Z is H; and  $X^-$  is H,  $CH_3SO_4$ ,  $C_2H_5SO_4$ 

is H, C<sub>1</sub> - C<sub>4</sub> alkyl groups or (CHY-CHZ<sub>D</sub>)OH where Y and Z are H or CH<sub>3</sub> provided that at least one of Y or Z is H; and X<sup>-</sup> is H, CH<sub>3</sub>SO<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>SO<sub>4</sub>, ½ SO<sub>4</sub>, HCO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub> or HOCH<sub>2</sub>COO and p is 1-5;

xi) compounds of the formula:

5

$$R^1$$
 $R^2$ 
 $N-R^3$ 

10

wherein R<sup>1</sup> and R<sup>2</sup> are C<sub>12</sub> - C<sub>22</sub> alkyl groups or alkenyl groups, R8CONHC<sub>m</sub>H<sub>2m</sub>, R9NHCOC<sub>m</sub>H<sub>2m</sub>, or R9OC<sub>m</sub>H<sub>2m</sub> wherein  $R^8$  is  $C_{11}$  -  $C_{21}$  alkyl or alkenyl groups,  $R^9$  is  $C_{12}$  -  $C_{22}$  alkyl or alkenyl groups and m is 1-5; R<sup>3</sup> and R<sup>4</sup> are H, C<sub>1</sub> - C<sub>4</sub> alkyl groups or (CHY-CHZD)OH where Y and Z are H or CH3 provided that at least one of Y or Z is H; and X- is H, CH3SO4, C2H5SO4, ½ SO4, HCO2, CH3CO2 or HOCH<sub>2</sub>COO and p is 1-5;

15

compounds of the formula: xii)

20

wherein  $R^5$  and  $R^6$  are  $C_{11}$  -  $C_{21}$  alkyl groups or alkenyl groups, R8COOC<sub>m</sub>H<sub>2m</sub>, R9OCOC<sub>m</sub>H<sub>2m</sub>, R8CONHC<sub>m</sub>H<sub>2m</sub>,  $R^9NHCOC_mH_{2m}$  or  $R^9OC_mH_{2m}$  wherein  $R^8$  is  $C_{11}$  -  $C_{21}$  alkyl or alkenyl groups, R9 is C12 - C22 alkyl or alkenyl groups and m is 1-5; R3 is H, C<sub>1</sub> - C<sub>4</sub> alkyl groups or (CHY-CHZ<sub>p</sub>)OH where Y and Z are H or CH3 provided that at least one of Y or Z is H; and X- is H, CH3SO4, C2H5SO4, 1/2 SO4, HCO2, CH3CO2 or HOCH2COO and p is 1-5; Q is O or NH; and n is 1-3;

lipophilic surfactants having a HLB of 6 or less; and

25

xiii) water repellents;

xiv) at least one of:

a)

30

b) propellants;

- xv) at least one of:
  - a) polymers or their salts prepared by polymerization of a monomer having at least a vinyl group and/or an aromatic ring, a sulfonic group and an average molecular weight of 10,000 to 500,000; and
  - b) carboxylic acid-containing polymers or salts thereof having recurring units of the formula [I]:

wherein X, Y and Z are each H, CH<sub>3</sub>, COOH or CH<sub>2</sub>COOH; and n is 10 to 2000; or of the formula [II]:

15

20

25

30

10

5

wherein m is 10-200;

- xv) swelling clay materials;
- xvi) alkalis;
  - xvii) gelatinous materials;
  - xviii) at least one of:
    - a) benzoic acid;
    - b) fluroescent brightening agents; and
  - c) perfumes;
  - xix) starch and starch derivatives.
- 2. The composition according to Claim 1 wherein said film-forming polymer is a water-soluble cellulose derivative or one or more substituted  $\beta$ -1,4-glucans, preferably selected from the group consisting of: carboxymethylcellulose, ethylhydroxyethylcellulose,

5

15

20

25

30

hydroxyethylcellulose, hydroxypropylcellulose, hydroxybutylcellulose, methylcellulose, methoxypropyl methyl cellulose, carboxymethylhydroxyethylcellulose, hexylcarboxymethyl cellulose, C<sub>12</sub> - C<sub>20</sub> alkyl carboxymethylcellulose, methylhydroxypropylcellulose, hydroxyethylmethylcellulose, hydroxypropylmethylcellulose, hydroxybutylmethylcellulose and mixtures thereof, more preferably selected from the group consisting of: hydroxypropylcellulose, hydroxypropylmethylcellulose, carboxymethylcellulose, hexylcarboxymethyl cellulose, C<sub>12</sub> - C<sub>20</sub> alkyl carboxymethylcellulose and mixtures thereof.

- 3. The composition according to Claim 1 wherein said fabric care composition provides stain and/or soil removal benefits to fabrics without inhibiting the clay stain removal properties of the fabric in a subsequent cleaning process.
  - 4. The composition according to Claim 1 wherein said film-forming polymer exhibits a viscosity of at least 5 Cp, preferably at least 10 Cp in a 2% by weight aqueous solution.
  - 5. The composition according to Claim 1 wherein said composition further comprises one or more quaternary ammonium compounds, preferably one or more biodegradable quaternary ammonium compounds, more preferably said one or more biodegradable quaternary ammonium compounds, when present, are present in said composition at a level of from 0.01% to 5% by weight of the composition.
  - 6. The composition according to Claim 1 wherein said film-forming polymer is present in said fabric care composition at a level of from 0.001% to 20%, preferably from 0.02% to 5%, more preferably from 0.05% to 2% by weight of the composition.
  - 7. A method for treating a fabric, preferably a garment, in need of treatment, said method comprising the step of contacting said fabric with a silicone- and starch-free fabric care composition comprising a film-forming polymer that forms a temporary film on said fabric such that stains that come into contact with said temporary film can be removed from said fabric upon washing.
  - 8. The method according to Claim 7 wherein said fabric care composition is applied to a fabric during a post-cleaning treatment process or to a new or clean fabric prior to wearing by a consumer.
  - 9. The method according to Claim 7 wherein said film-forming polymer is a water-

soluble cellulose derivative or one or more substituted β-1,4-glucans, preferably selected from the group consisting of: carboxymethylcellulose, ethylhydroxyethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxypropyl methyl cellulose, hydroxybutylcellulose, methylcellulose, methoxypropyl methyl cellulose, carboxymethylhydroxyethylcellulose, hexylcarboxymethyl cellulose, C<sub>12</sub> - C<sub>20</sub> alkyl carboxymethylcellulose, methylhydroxyethylcellulose, methylhydroxypropylcellulose, hydroxyptylmethylcellulose, hydroxypropylmethylcellulose, hydroxybutylmethylcellulose and mixtures thereof, more preferably selected from the group consisting of: hydroxypropylcellulose, hydroxypropylmethylcellulose, carboxymethylcellulose, hexylcarboxymethyl cellulose, C<sub>12</sub> - C<sub>20</sub> alkyl carboxymethylcellulose and mixtures thereof.

- The method according to Claim 7 wherein said fabric care composition further comprises one or more quaternary ammonium compounds, preferably one or more biodegradable quaternary ammonium compounds, more preferably said one or more biodegradable quaternary ammonium compounds, when present, are present in said composition at a level of from 0.01% to 5% by weight of the composition.
- The method according to Claim 7 wherein said film-forming polymer is present on the surface of said treated fabric at a level of at least 0.01 g/m<sup>2</sup>, preferably from 0.05 g/m<sup>2</sup> to 10 g/m<sup>2</sup>.
  - 12. The method according to Claim 7 wherein said film-forming polymer is present in said fabric care composition at a level of from 0.001% to 20%, preferably from 0.02% to 5%, more preferably from 0.05% to 2% by weight of the composition.
  - 13. The method according to Claim 7 wherein said film-forming polymer exhibits a viscosity of at least 5 Cp, preferably at least 10 Cp in a 2% by weight aqueous solution.
- The method according to Claim 7 wherein said fabric care composition is applied to said fabric by a spray application, preferably by a non-aerosol spray application.
  - 15. A silicone- and starch-free fabric care composition comprising:
    - a) from 0.02% to 5% of a film-forming polymer;
- b) from 0.01% to 5% of a quaternary ammonium compound;
  - c) optionally, from 0.01% to 80% adjunct materials; and

d) balance solvent wherein said solvent is selected from the group consisting of water, alcohol, polyethylene glycol and mixtures thereof;

wherein said weight ratio of said film-forming polymer to quaternary ammonium compound is from 50:1 to 1:5.

5

10

- 16. An article of commerce comprising a container containing a silicone- and starch-free fabric care composition comprising a film-forming polymer, which forms a temporary film on fabrics such that stains that come into contact with said temporary film can be removed from said fabric upon washing; wherein said container includes instructions for protecting fabrics from stains comprising the instruction to apply said fabric care composition to the surface of a fabric in need of treatment.
- 17. The article according to Claim 16 wherein said instructions further comprise applying said fabric care composition to the surface of a fabric in need of treatment during a post-cleaning treatment process.
  - 18. A fabric care composition comprising:
    - a) a film-forming polymer; and
    - b) a biodegradable quaternary ammonium compound, and
- 20 c) optionally, but preferably a nonionic surfactant having an HLB value of 8-14, and
  - d) optionally, but preferably a perfume.
  - 19. A fabric care composition comprising:
- a) a film-forming polymer; and
  - b) a nonionic surfactant having an HLB value of 8-14.
  - 20. A fabric care composition comprising:
    - a) a film-forming polymer; and
- 30 b) a perfume.
  - 21. A method for protecting a surface against soiling, said method comprising the step of contacting said surface with a surface care composition comprising a film-forming polymer that forms a temporary film on said surface such that stains that come into contact with said temporary film can be removed from said surface upon washing.

22. A method for treating a surface in need of treatment, said method comprising the step of contacting said surface with a surface care composition comprising a film-forming polymer that forms a temporary film on said surface such that stains that come into contact with said temporary film can be removed from said surface upon washing.

#### (19) World Intellectual Property Organization International Bureau



# 

(43) International Publication Date 2 November 2000 (02.11.2000)

#### (10) International Publication Number WO 00/65015 A3

- (51) International Patent Classification7: C11D 3/22. 1/62, 11/00, 3/00, 17/00, B08B 17/00, C09D 5/00, C11D 1/72, 3/50
- (21) International Application Number: PCT/US00/11056
- (22) International Filing Date: 25 April 2000 (25.04.2000)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 60/131.288

27 April 1999 (27.04.1999) US

- (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): BETTIOL, Jean-Luc, Philippe [FR/BE]; 93. Avenue J, Slegers, B-1200 Brussels (BE). VERSCHUERE, Ann, Katrien, Marie, Agnes [BE/BE]; Asselsstraat 102, B-9031 Drongen (BE). BAECK, Andre, Cesar [BE/BE]; Prusessteenweg 273, B-2820 Bonheiden (BE), SMETS, Johan [BE/BE]; Bollenberg 79, B-3210 Lubeck (BE), BUSCH, Alfred [DE/DE]; Handelsstraat 210, B-2910 Londerzeel (DE). COOREMANS, Steven, Paul, Georges [BE/BE]; Kasteelstraat 224, B-9255 Buggenhout (BE).

- (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).
- (81) Designated States (national): AE, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN. CR, CU, CZ, CZ (utility model), DE, DE (utility model). DK, DK (utility model), DM, EE, EE (utility model), ES. FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID. IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL. PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model). SL. TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

#### Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- (88) Date of publication of the international search report: 8 February 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

# (54) Title: SURFACE CARE COMPOSITIONS AND METHODS FOR TREATING SURFACES

(57) Abstract: The present invention relates to a surface care composition, preferably a fabric care composition to be applied on a new and/or clean surface, preferably fabric surface, fully or in discrete regions thereof, comprising a film-forming polymer and providing superior soil removal performance while maintaining the particulate stain removal performance. The present invention further relates to a process of treating a new and/or clean surface, preferably fabric surface, fully or in discrete regions thereof with such composition, to impart soil release properties thereto.

International Application No

PCT/US 00/11056 A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/22 C11D1/62 C11D17/00 C11D3/00 C11D11/00 C11D1/72 C11D3/50 C09D5/00 B08B17/00 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED  $\begin{array}{ccc} \text{Minimum documentation searched} & \text{(classification system tollowed by classification symbols)} \\ IPC 7 & C11D & B08B & C09D \end{array}$ Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) WPI Data, PAJ, EPO-Internal C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No.

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Helevant to claim No.
X	DATABASE WPI Section Ch, Week 198403 Derwent Publications Ltd., London, GB; Class A87, AN 1984-015535 XP002145503 & JP 58 056600 B (MATSUMOTO SENI KAGA), 15 December 1983 (1983-12-15) abstract	1,6-8, 14,16, 17,21,22
X	US 4 136 038 A (PRACHT HANS J ET AL) 23 January 1979 (1979-01-23)  column 3, line 62 -column 4, line 9; claims 6-10; example III column 7, line 5 - line 45	1-4, 6-15,21, 22
	-/	

Further documents are listed in the continuation of box C.	Patent family members are listed in annex.
<ul> <li>Special categories of cited documents:</li> <li>"A" document defining the general state of the art which is not considered to be of particular relevance</li> <li>"E" earlier document but published on or after the international filing date</li> <li>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</li> <li>"O" document referring to an oral disclosure, use, exhibition or other means</li> <li>"P" document published prior to the international filing date but later than the priority date claimed</li> </ul>	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  "&" document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report
30 August 2000	0 4. 12. 00
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentiaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  Fax: (+31-70) 340-3016	Authorized officer  Loiselet-Taisne, S

Ints...ational Application No PCT/US 00/11056

- · · ·		PCT/US 00	11020
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.
X	US 5 017 237 A (SVENSSON SIGFRID) 21 May 1991 (1991-05-21) column 1, line 6 - line 15; claim 1; example 8		1-4,21,
X	US 3 928 213 A (TEMPLE ROBERT DWIGHT ET AL) 23 December 1975 (1975-12-23)  column 10, line 56 -column 57; claims 1-10; example II column 7, line 21 - line 45		1-4,6-9, 12,13, 19,21,22
Х	GB 1 604 562 A (UNILEASE) 9 December 1981 (1981-12-09) claims 1,12,17,19; examples 1,2		1,2,6, 21,22
х	PATENT ABSTRACTS OF JAPAN vol. 009, no. 041 (C-267), 21 February 1985 (1985-02-21) & JP 59 186668 A (FUROINTO SANGYO KK), 23 October 1984 (1984-10-23) abstract		1,2,7-9, 14,16, 17,21,22
			•
		·	
·			
			•
			·

11

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

international application No. PCT/US 00/11056

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)
Observations where certain claims were round unsearchable (Continuation of item 1 of first sheet)
This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2. X Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  See FURTHER INFORMATION sheet PCT/ISA/210
3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows:
see additional sheet
As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  partially 1-4, 6-9, 11-14, 16, 17, 21-22
Remark on Protest  The additional search fees were accompanied by the applicant's protest.  No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

### FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

#### Continuation of Box I.2

In view of the wording of the claims presently on file, which render it difficult, if not impossible, to determine the matter for which protection is sought, the present application fails to comply with the clarity and conciseness requirements of Article 6 PCT (see also Rule 6.1(a) PCT) to such an extent that a meaningful search is impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear (and concise).

The subject-matter for which protection is sought should be described by the technical feature of the invention (Art.6; Rule 6.3a PCT). The only positive feature of claim 1 is "a film-forming polymer". Features defining what is not the subject-matter for which protection is sought cannot contribute to formulating a meaningful search. The above feature merely reflect the underlying technical problem to be solved.

The claims cover all compositions having this disclaimer, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such compositions. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Moreover, the incorporation of non-limiting negative features extended in over several pages renders the set of claims as a whole inconsise (Art.6 second sentence PCT).

Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed (Art.6 PCT, 3rd sentence; Rule 5.1(a)(iii) PCT), namely the those parts relating to a film-forming polymer as defined in claim 2 well supported by the description (see p.18 5d paragraph and the examples).

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: partially 1-4, 6-9, 11-14, 16, 17, 21-22

Fabric care composition characterised by a film-forming polymer only.

Method for treating surface in need of treatment or for protecting a surface against soil, said method comprising the step of contacting said surface with a care composition as above defined that forms a temporary film on said surface such that stains that come into contact with said temporary film can be removed from said surface upon washing;

Article of commerce comprising a container containing a fabric care composition as here above defined, free of silicone and starch

2. Claims: 5, 10, 15, 18 and partially 1-4, 6-9, 11-14, 16, 17, 21-22

Fabric care composition comprising: a) a film-forming polymer, b) a quaternary ammonium compound;

Method for treating surface in need of treatment or for protecting a surface against soil, said method comprising the step of contacting said surface with a care composition as here above defined that forms a temporary film on said surface such that stains that come into contact with said temporary film can be removed from said surface upon washing;

Article of commerce comprising a container containing a fabric care composition as here above defined, free of silicone and starch.

3. Claims: 19 and partially 1-4, 6-9, 11-14, 16-17, 21-22

Fabric care composition comprising: a) a film-forming polymer and b) a nonionic surfactant having an HBL value of 8-14.

Method for treating surface in need of treatment or for protecting a surface against soil, said method comprising the step of contacting said surface with care composition as here above defined, that forms a temporary film on said surface such that stains that come into contact with said temporary film can be removed from said surface upon washing;

Article of commerce comprising a container containing a

# FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

fabric care composition, as here above defined, free of silicone and starch.

4. Claims: 20 and partially 1-4, 6-9, 11-14, 16-17, 21-22

Fabric care composition comprising: a) a film-forming polymer and b) perfume.

Method for treating surface in need of treatment or for protecting a surface against soil, said method comprising the step of contacting said surface with care composition as here above defined, that forms a temporary film on said surface such that stains that come into contact with said temporary film can be removed from said surface upon washing;

Article of commerce comprising a container containing a fabric care composition, as here above defined, free of silicone and starch.

Information on patent family members

					PCT/	PCT/US 00/11056	
	itent document I in search report	t 	Publication date		Patent family member(s)	Publication date	
JP	58056600	В	23-09-1975	JP	50121600 A	23-09-1975	
US	4136038	Α	23-01-1979	CA	1090059 A	25-11-1980	
US	5017237	Α	21-05-1991	AT	127500 T	15-09-1995	
				AT	74293 T	15-04-1992	
				AU	615662 B	10-10-1991	
				AU	1958888 A	19-01-1989	
				AU	612163 B	04-07-1991	
				AU	1959288 A	19-01-1989	
				BR CA	8807569 A 1294182 A	10-04-1990	
				CA	1318988 A	14-01-1992 15-06-1993	
				DE	3854432 D	12-10-1995	
				DE	3854432 T	02-05-1996	
			•	DE	3869778 A	07-05-1992	
				DE	3869778 D	07-05-1992	
				DK	637589 A	13-02-1990	
				EP	0366704 A	09-05-1990	
				EP FI	0365584 A 93221 B	02-05-1990	
				JР	93221 B 2503927 T	30-11-1994 15-11-1990	
				JР	2766653 B	18-06-1998	
			•	JP	2503881 T	15-11-1990	
				JP	2635144 B	30-07-1997	
				NO	177666 B	24-07-1995	
			•	SE	466639 B	16-03-1992	
		•		SE WO	8704589 A 8810284 A	18-12-1988	
				WO	8810284 A 8810156 A	29-12-1988 29-12-1988	
				SE	462319 B	11-06-1990	
				SE	8904238 A	15-12-1989	
				US	5093485 A	03-03-1992	
US	3928213	A	23-12-1975	AT	347552 B	10-01-1979	
				AT BE	239574 A 812785 A	15-05-1978	
				CA	812785 A 1024703 A	25-09-1974 24-01-1978	
				CA	1027713 A	14-03-1978	
				CH	603788 A	31-08-1978	
	•			DE	2413042 A	10-10-1974	
			•	FR	2222476 A	18-10-1974	
				GB	1459935 A	31-12-1976	
				IT JP	1005781 B 50035495 A	30-09-1976	
				NL	7403897 A	04-04-1975 25-09-1974	
CD	1604560		00 10 100				
GB	1604562	Α	09-12-1981	DE	2723493 A	30-11-1978	
				AT AT	373794 B 362278 A	27-02-1984	
				BE	867438 A	15-07-1983 18-09-1978	
	•			CH	621071 A	15-01-1981	
				DK	230078 A	26-11-1978	
				FR	2391784 A	22-12-1978	
	•			LU	79698 A	06-11-1978	
				NL	7805662 A	28-11-1978	
				SE	438322 B	15-04-1985	
				SE	7805937 A	26-11-1978	

International Application No

INTERNATIONAL SEARCH REPORT International Application No Information on patent family members PCT/US 00/11056 Patent document Publication Patent family member(s) Publication cited in search report date date JP 59186668 Α 23-10-1984 NONE

Form PCT/ISA/210 (patent family annex) (July 1992)

THIS PAGE BLANK (USPTO)